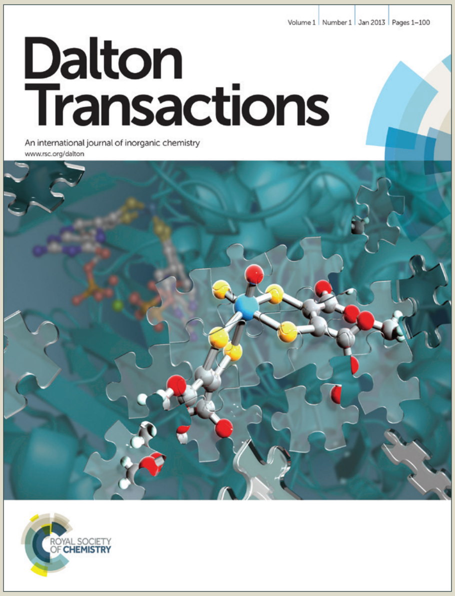
Dalton Transactions

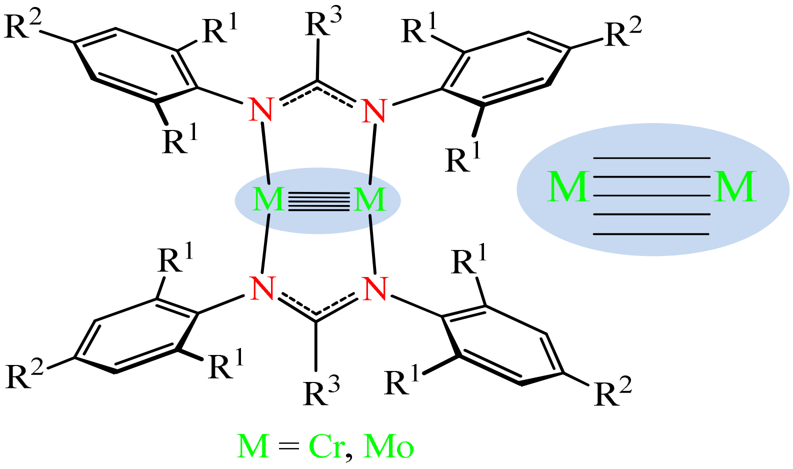
Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/dalton

Graphical Abstract



Recent achievements in the area of the metal-metal quintuple bonding are highlighted, including synthesis of the quintuple bonded complexes, the metal-to-metal bonding schemes, and their reactivity.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Theory, Synthesis and Reactivity of Quintuple Bonded Complexes

Anokh K. Nair, N. V. Satyachand Harisomayajula and Yi-Chou Tsai*

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

This perspective reviews recent advances in the newly discovered metal-to-metal quintuple bonded complexes. The idea of the structures of the metal-metal quintuple bonded complexes was initiated by theoreticians in 1979 and 2001 based on two types of model compounds, the D_{3h} M_2L_6 and *trans-bent* M_2H_2, respectively. This theoretical hypothesis was put into practice in 2005 with the preparation of the first isolable quintuple bonded chromium terphenyl dimer $Cr_2Ar'_2$ (Ar' = 2,6-(2,6-*i*-$Pr_2C_6H_3)_2C_6H_3$). After this landmark discovery, many N-based donor-stabilized dinuclear group 6 quintuple bonded complexes with very short metal-metal separations have been identified by X-ray crystallography, and their quintuple bonding was corroborated by magnetic measurements and theoretical calculations. Unlike the quadruple bonded bimetallic units uniformly supported in a tetragonal environment, the configuration of the characterized quintuple bonded dinuclear complexes varies with the ligands and metals. Three types of quintuple bonded complexes have been identified up to date. In addition to their geometry variation and interesting bonding schemes, these low-valent and low-coordinate quintuple bonded complexes are highly reducing and have been shown reactive towards small inorganic molecules and unsaturated organics.

Anokh K. Nair was born in Kerala, India, in 1988. He received his BSc from Mahathma Gandhi University in 2008 and MSc from National Institute of Technology, Tiruchirappalli, India in 2010. He is presently a PhD student in Professor Yi-Chou Tsai's group in the Department of Chemistry and Frontier Research Center on Fundamental and Applied Sciences of Matters at National Tsing Hua University. His research interests encompass organic synthesis, synthesis, characterization, and reactivity studies of multiple bonded dinuclear transition metal complexes.

Naga Venkata Satyachand Harisomayajula received his BSc from Andhra University, and his MSc in 2006 from Andhra University, India. Upon graduation, he went to industry and worked as a Research Scientist for five years. He is currently a PhD student under the supervision of Professor Yi-Chou Tsai in the Department of Chemistry and Frontier Research Center on Fundamental and Applied Sciences of Matters at National Tsing Hua University. His research interest lies in exploring the low-coordinate and low-valent multiple bonded dinuclear complexes.

Yi-Chou Tsai obtained his BSc and MSc degrees from the Department of Chemistry, National Taiwan Normal University in Taiwan and his PhD degree from MIT. After a two-year postdoctoral fellowship at Caltech, he joined the Department of Chemistry at National Tsing Hua University in 2003, where he is currently a full professor. His research interest is focused in inorganic and organometallic synthesis, particularly in the synthesis, isolation, and characterization of unusually reactive dinuclear transition metal complexes of unique design and construction.

Introduction

Bonding theory in molecules of main group elements was initiated by Lewis with his electron-dot diagrams in the early 20th century.[1] The chemistry of multinuclear transition metal complexes developed in the period of 1963-1965 was the starting point of metal-to-metal multiple bond chemistry.[2] The conventional outlook of chemical valency and bond order were questioned after the recognition of the first metal-metal quadruple bond in $[Re_2Cl_8]^{2-}$ by Cotton's group in 1964.[3] According to the basic principles, it is clear that a pair of electrons can form a covalent bond. Hence, it is possible to form up to nine bonds between two transition metal atoms by the participation of all the valence s, p, and d orbitals.[4] This increases the scope of going beyond the quadruple bond. Theoretical investigations on the sextuple bonded simple diatomic molecules Cr_2 and Mo_2[5-11] and quintuple bonded Nb_2,[12] probed from metal atom-argon matrix condensation experiments, had given more in-depth knowledge about the bonding pattern. The valence electronic configuration of the group 6 metal atoms is $ns^1(n\text{-}1)d^5$, so their diatomic M_2 molecules could potentially have six bonding orbitals, namely 2 σ, 2 π and 2 δ, as illustrated in Figure 1. In addition, in view of the identification of a large number of quadruple bonded bimetallic compounds, it has become apparent that the quintuple bonded complexes were likely to be experimentally achieved.

((Fig. 1))

The first report on the metal-metal quintuple bond was made by Hoffmann et al. in 1979, who suggested that the metal-metal quintuple bonded dinuclear species could potentially exist with a D_{3h} configuration.[13] In 2001, the *trans*-bent geometry of M_2H_2 was predicted for group 6 metals allowing for the quintuple bond formation in theoretical calculations of Landis and Weinhold, which was an important step in the field of quintuple bond chemistry.[14-17] The *trans*-bent configuration comes forth as a result of the hybridization tendencies of *s* and *d* orbitals of transition metals, and such hybridization results in strong M-M σ bonds and bent ligand arrangements about the metal.[18-21] Compared to other transition metals, the group 6 elements in the hypothetical *trans*-bent M_2H_2 ensures a regular trend in its metal-metal bond length. That is, the bond lengths of the M-M quintuple bond and M-H bond increase from Cr to W.[15] Besides the *trans*-bent configuration, one interesting theoretical study on quintuple bonding was reported by Hoffmann et al. in 2007. By investigating the model complexes RMMR (M = Cr, Mo, W; R = H, F, Cl, Br, CN and Me), they suggested the possibility of other configurations, such as *trans*-bent with one of the R groups in a bridging fashion, lower symmetry C_s, linear geometry etc., for the existence of the quintuple bond. The *cis*-bent geometry was less likely due to steric repulsion.[22]

In theory, in quintuple bonded dinuclear compounds, each metal fragment should attain a configuration, in which all five d orbitals of the metal centre are singly occupied as shown in Figure 2. As the spin state of a metal complex is strongly influenced by the field strength of the ancillary ligands, the use of strong σ-donor and π-acceptor ligands should be avoided in this regard. Furthermore, to increase the overlap between d orbitals and to reduce the participation of the metal d orbitals in σ and π bonding to the ligands, the number of ligands must be minimized and π-donor ligands should be obviated as well. In brief, the metal centres should feature low coordination number (C.N.) with respect to the ligands and minimum metal valency to form quintuple bonded complexes. For a long time, there has been no substantial experimental progress in the field of quintuple bond chemistry until the milestone achievement of the first isolable quintuple bonded dimeric chromium aryl complex Ar'CrCrAr' (Ar' = 2,6-(2,6-*i*-$Pr_2C_6H_3)_2C_6H_3$) (**1**) by Power and co-workers in 2005.[23] This exciting breakthrough led to a wide horizon of this field through a number of bimetallic group 6 quintuple bonded complexes characterized by the Tsai,[24-27] Theopold,[28] Kempe[29] and Lu[30] groups. Noteworthy is that each group used different sterically demanding ligands to support the quintuple bonded bimetal units, but carbon and nitrogen donor-based ligands overwhelmingly predominate in this field.[31,32] As illustrated in Figure 2, there are four types of geometries for quintuple bonded complexes. The type *I* is theoretically the most acceptable, and type *II*-*IV* are structurally identified. Tsai, Kempe and Theopold's groups identified a number of type *II* dichromium and dimolybdenum complexes with very short metal-metal bonds spanned by two bidentate nitrogen based ligands. Furthermore, Tsai and Lu reported type *III* and type *IV* quintuple bonded complexes.[30, 33, 34] Interestingly, the shortest Cr-Cr quintuple bond length was recently disclosed by Kempe and co-workers by employing very sterically encumbering guanidinate ligands.[35, 36]

((Fig. 2))

Another conspicuous asset of quintuple bonded complexes is their remarkable reactivity, because of their low-coordinate and low-valent bimetal units. For example, quintuple bond destruction,[37] activation of small inorganic molecules[38-40] and alkene- and alkyne-like reactions, such as carboalumination,[41] cycloaddition reactions[42-44] and Friedel-Crafts-like haloacylation,[45] are the major reactivity studies achieved yet. In this perspective, we embark on a journey through the ligand selection, synthetic pathways, and the conformation of quintuple bonded complexes, and their bonding schemes[46-48] and remarkable reactivity.

Synthesis

In the field of the quintuple bond chemistry, synthesis means stabilization of a quintuple bonded bimetal moiety with specially designed ligands. After Power's success in assembling the quintuple bonded Cr_2^{2+} units with two monovalent bulky terphenyl ligands 2,6-(2,6-*i*-$Pr_2C_6H_3)_2C_6H_3$, a number of bimetallic quintuple bonded complexes were subsequently characterized. The common pathway for the synthesis of the quintuple bonded complexes is demonstrated in Scheme 1, where a halide containing metal complex, obtained from the reactions of anionic ligand with metal halide precursors, undergoes reduction to give the quintuple bonded complexes. This was the only protocol for the construction of the quintuple bonded complexes until an unconventional method reported by Tsai in 2012, in which such metal-halide complex was not formed, and subsequent reduction still results the isolation of the quintuple bonded complex.

((Scheme 1))

Synthetic method A

Although the above principle has been effectively adopted for quintuple bonded species, divergent synthetic pathways of these quintuple bonded complexes have been developed by judicious selection of appropriate metal precursors and ligand scaffolds, which are the crucial factors bringing the variety.

Power's dimeric chromium terphenyl complexes Ar'CrCrAr' (Ar' = C_6H_2-2,6-(2,6-*i*-$Pr_2C_6H_3)_2$-4-R) (**1**: R = H; **2**: R = $SiMe_3$; **3**: R = OMe; **4**: R = F) bearing a Cr-Cr quintuple bond were synthesized by the method analogous to Wurtz reductive coupling.[49] Treatment of $CrCl_2(THF)_2$ with four bulky terphenyl ligand C_6H_2-2,6-(2,6-*i*-$Pr_2C_6H_3)_2$-4-R (**20**: R = H; **21**: R = $SiMe_3$; **22**: R = OMe; **23**: R = F)[50] afforded the dichloro bridged dichromium complexes (Ar'Cr(μ-Cl))$_2$ (**24**: R = H; **25**: R = $SiMe_3$; **26**: R = OMe; **27**: R = F), which underwent KC_8 reduction to yield the quintuple bonded complexes **1-4**[23,51] (Scheme 2).

((Scheme 2))

Following Power's landmark discovery of **1**, Theopold and co-workers described the synthesis of a diazadiene supported quintuple bonded dichromium complex in 2007.[28] As illustrated in Scheme 3, by mixing $CrCl_3(THF)_3$ and $Na_2[^{H}L^{i\text{-}Pr}]$ ($^{H}L^{i\text{-}Pr}$ = N-N'-bis(2,6-*i*-$Pr_2C_6H_3$)-1,4-diazadiene) (**28**), they were able to isolate the dicholor-bridged dinuclear species [$^{H}L^{i\text{-}Pr}$Cr(μ-Cl)] (**29**). KC_8 reduction of **29** gave rise to the formation of the red-green quintuple bonded dichromium complex [μ-κ^2-(HCN-2,6-*i*-$Pr_2C_6H_3)_2Cr]_2$ (**5**).

((Scheme 3))

Tsai and co-workers have employed the simple amidinato ligands $[HC(NAr)_2]^-$ for the preparation of the quintuple bonded dinuclear compounds. One of the merits of using amidinates as supporting ligands is their poor π-donating nature, which can minimize the metal-ligand π bonding interactions, and consequently maximise the metal-metal interactions. For example, they reduced the bis(μ-amidinato)di(μ-chloro)dichromium complex [{Cr(THF)}(μ-Cl){μ-κ^2-(HC(N-2,6-$Me_2C_6H_3)_2$)}]$_2$ (**30**) with KC_8,[52] and they unexpectedly isolated the paramagnetic mixed-valent Cr_2^{3+} complex Cr_2(μ-κ^2-(HC(N-2,6-$Me_2C_6H_3)_2))_3$ (**31**) with a formal Cr-Cr bond order of 4.5. Subsequent one electron-reduction of **31** resulted in the characterization of the quintuple bonded complex $[Cr_2(\mu\text{-}ArNC(H)NAr)_3]^-$ (**6**). These two complexes are apt examples of the type *III* lantern type conformation (Scheme 4).[24]

((Scheme 4))

Later on, Tsai and co-workers described the synthesis of four amidinate-supported type *II* complexes [Cr{R'C(NAr)$_2$}]$_2$ (**7**: R' = H, Ar = 2,4,6-$Me_3C_6H_2$; **8**: R' = H, Ar = 2,6-$Et_2C_6H_3$; **9**: R' = H, Ar = 2,6-*i*-Pr_2-C_6H_3; **10**: R' = H, Ar = 2,6-*i*-Pr_2-C_6H_3)[25] (Figure 3). The synthetic routes of **7-10** are similar. As presented in Scheme 5, reactions of $CrCl_3$ and the lithiated amidinates Li[R'C(NAr)$_2$] (**32**: R' = H, Ar = 2,4,6-$Me_3C_6H_2$; **33**: R' = H, Ar = 2,6-$Et_2C_6H_3$; **34**: R' = H, Ar = 2,6-*i*-Pr_2-C_6H_3 ; **35**: R' = H, Ar = 2,6-*i*-Pr_2-C_6H_3) in THF gave the green paramagnetic (3 unpaired electrons for each) mononuclear compounds $CrCl_2(THF)_2$[R'C(NAr)$_2$] (**36**: R' = H, Ar = 2,4,6-$Me_3C_6H_2$; **37**: R' = H, Ar = 2,6-$Et_2C_6H_3$; **38**: R' = H, Ar = 2,6-*i*-Pr_2-C_6H_3; **39**: R' = H, Ar = 2,6-*i*-Pr_2-C_6H_3). Upon reduction of **36-39** by KC_8, the orange-red quintuple bonded chromium dimers **7-10** were isolated in good yields.

((Fig. 3))

((Scheme 5))

Tsai and co-workers prepared the first Mo-Mo quintuple bonded complexes in 2009 by reducing the paddlewheel quadruple bonded dimolybdenum complexes Mo_2(μ-Cl)[(μ-Cl)$_2$Li(OEt$_2$)][μ-κ^2-RC(N-2,6-*i*-$Pr_2C_6H_3)_2]_2$ (**42**: R = H; **43**: R = Ph) with sterically demanding amidinates RC(N-2,6-*i*-$Pr_2C_6H_3)_2$ (**40**: R = H; **41**: R = Ph).[26] As shown in Scheme 6, treatment of $K_4Mo_2Cl_8$ with 2 equivalents of amidinate **40** and **41** in THF produced **42** and **43**, which are structurally similar with a Cl-Li-Cl linkage spanning the Mo-Mo quadruple bond. Subsequent reduction of **42** and **43** led to the isolation of Mo-Mo quintuple bonded complexes [Mo(μ-κ^2-RC{N-2,6-*i*-$Pr_2C_6H_3$}$_2$)]$_2$ (**13**: R = H; **14**: R = Ph). Interestingly, an alternative synthetic pathway of **12** through photolysis of the quadruple bonded dimolybdenum dihydride amidinate [Mo(H)(THF)(μ-κ^2-HC{N-2,6-*i*-$Pr_2C_6H_3$}$_2$]$_2$ was recently described by Carmona in 2013.[53]

((Scheme 6))

Mono-anionic amidopyridine and guanidinate ligands were also utilized by the Kempe's group to stabilize Cr-Cr quintuple bonds. Two reactions were carried out by mixing $CrCl_3(THF)_3$ with a mixture of KH and aminopyridine 2-(HN-2,4,6-$Me_3C_6H_2$)-4-(2,4,6-*i*-$Pr_3C_6H_2$)C_5H_3N] (**44**) and $CrCl_2$ with a mixture of *n*-BuLi with **44** to give the mononuclear [$CrCl_2(THF)_2${2-(N-2,4,6-$Me_3C_6H_2$),4-(2,4,6-*i*-$Pr_3C_6H_2$)}C_5H_5N] (**45**) the dinuclear species [Cr(THF)(μ-Cl)(2-(N-2,4,6-Me_3-C_6H_2)-6-(N-2,4,6(*i*-$Pr_3)_2C_5H_3N]_2$ (**46**), respectively. Interestingly, though **45** and **46** are structurally different, subsequent KC_8 reduction of both resulted in the formation of the quintuple bonded Cr dimer [Cr(μ-κ^2-{2-N(2,4,6-$Me_3C_6H_2$)-4-(2,4,6-*i*-$Pr_3C_6H_2$)}$C_5H_3N]_2$ (**11**)[29] (Scheme 7). The tendency of guanidinate ligands to stabilize short metal-metal bonds has been demonstrated by Cotton et al,[54] paving the way for the Kempe's group to prepare the yet shortest Cr-Cr quintuple bonds supported by bulky guanidinate ligands. Mixing the lithium guanidinate Li[RC(N-2,6-*i*-$Pr_2C_6H_3)_2$] (R = Me_2N (**47**), 2,6-$Me_2C_5H_8N$ (**48**)) with $CrCl_2$ in THF yielded the dimeric Cr(II) complex [Cr(μ-Cl)(κ^2-Me_2NC(N-2,6-*i*-$Pr_2C_6H_3)_2$)]$_2$ (**49**) and the monomeric Cr(II) -ate complex [(κ^2-$Me_2C_5H_8NC$(N-2,6-*i*-$Pr_2C_6H_3)_2$)Cr(μ-Cl)$_2$[Li(THF)$_2$]] (**50**), respectively. Subsequent KC_8 reduction of **49** and **50** resulted in the formation of the quintuple bonded dimer $[Cr(\mu\text{-}\kappa^2\text{-}RC(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_2)]_2$ (R = Me_2N (**15**), 2,6-$Me_2C_5H_8N$ (**16**)) (Scheme 8).[35, 36]

((Scheme 7))

((Scheme 8))

In 2012, Tsai and co-workers reported a lantern-type quintuple bonded dimolybdenum trisamidinate complex, wherein, besides bridging amidinato ligands, the Mo_2 unit is spanned by a Li atom, from an interesting synthetic route. As shown in Scheme 9, reaction of 2 equivalent of lithium amidinate ligand $Li[HC(N\text{-}2,6\text{-}Et_2(C_6H_3)]$ (**51**) with $Mo_2Cl_6(THF)_3$ in the presence of zinc powder produced a diamagnetic trimolybdenum complex $[Mo_2\{\mu\text{-}HC(N\text{-}2,6\text{-}Et_2C_6H_3)\}_2(\mu\text{-}Cl)\{(\mu\text{-}Cl)_2Mo(\mu\text{-}Cl)_2Li(THF)(OEt_2)\}]$ (**52**), which contains a quadruple bonded Mo_2 unit. The quadruple bonded complex **52** underwent reduction with 2 equivalent of KC_8 to yield the diamagnetic '-ate' complex $[Mo_2\{\mu\text{-}HC(N\text{-}2,6\text{-}Et_2C_6H_3)\}_2(\mu\text{-}Cl)\{(\mu\text{-}Cl)_2Li(THF)_2]$ (**53**). After reduction of **52** and **53** with 2 and 4 equivalent of KC_8, respectively, the novel Mo-Mo quintuple bonded complex $[Mo_2(\mu\text{-}Li)\{\mu\text{-}HC(N\text{-}2,6\text{-}Et_2C_6H_3)\}_2]$ (**17**) was isolated in low yields (11-17%), presumably due to complicated ligand redistribution processes.[33]

((Scheme 9))

In 2013, Lu achieved the synthesis of the first heterodinuclear quintuple bonded complex $[MnCr(N(o\text{-}(i\text{-}Pr_2PCH_2N)C_6H_4)_3)]$ (**19**), containing a quintuple bonded CrMn unit.[30] With the employment of the dinucleating double-decker heptadentate tris(phosphinoamido)amine ligand $N(o\text{-}(i\text{-}Pr_2PCH_2N)C_6H_4)_3$, the Lu's group has been able to assemble a number of multiple bonded heterobimetallic complexes through a stepwise fashion.[55,56] As presented in Scheme 10, after deprotonation by *n*-BuLi, the dinuclear double-decker ligand $[N(o\text{-}(i\text{-}Pr_2PCH_2N)C_6H_4)_3]^{3-}$ (**54**) was added to $CrCl_3$, and the monometalated complex $[Cr(N(o\text{-}(i\text{-}Pr_2PCH_2N)C_6H_4)_3]$ (**55**) was isolated, which was subsequently treated with $MnCl_2$ and then reduced by KC_8 in THF resulting in the quintuple bonded heterobimetallic complex **19**.[30]

((Scheme 10))

Synthetic method B

All the above stated synthetic pathways for quintuple bonded dinuclear complexes are similar to the Wurtz reductive coupling reaction.[49] Recently, Tsai reported an non-halide method to prepare a quintuple bonded dichromium complex. As illustrated in Scheme 11, the halide-free dimeric homodivalent chromium pyridyldiamide complexes $[(THF)Cr(\mu\text{-}\kappa^1\text{:}\kappa^2\text{-}2,6\text{-}(2,6\text{-}i\text{-}Pr_2C_6H_3\text{-}N)_2\text{-}4\text{-}CH_3C_5H_2N)]_2$ (**58**) and $[(THF)Cr(\mu\text{-}\kappa^1\text{:}\kappa^2\text{-}2,6\text{-}(i\text{-}Pr_3Si\text{-}N)_2C_5H_3N)]_2$ (**59**) were prepared using the 2,6-diamidopyridine derivatives $[(2,6\text{-}i\text{-}Pr_2C_6H_3\text{-}N)_2\text{-}4\text{-}CH_3C_5H_2N)]^{2-}$ (**56**) and $[2,6\text{-}(i\text{-}Pr_3Si\text{-}N)_2C_5H_3N)]^{2-}$ (**57**). Subsequent one-electron reduction of both **58** and **59** produced the mixed-valent complexes $[(Et_2O)K@18\text{-}crown\text{-}6][Cr^I\{\mu\text{-}\kappa^1\text{:}\kappa^2\text{-}2,6\text{-}(2,6\text{-}i\text{-}Pr_2C_6H_3\text{-}N)_2\text{-}4\text{-}CH_3C_5H_2N\}_2Cr^{II}]$ (**60**) and $[(THF)_2K@18\text{-}crown\text{-}6][Cr^I\{\mu\text{-}\kappa^1\text{:}\kappa^2\text{-}2,6\text{-}(i\text{-}Pr_3Si\text{-}N)_2C_5H_3N\}_2Cr^{II}]$ (**61**). Both **60** and **61** contain a linear two-coordinate monovalent chromium[57] and a distorted square planar four-coordinate divalent chromium centre. Further KC_8 reduction of **60** gave the burgundy diamagnetic quintuple bonded dichromium complex $[\{(Et_2O)K\}_2\{Cr_2(\mu\text{-}\kappa^1\text{:}\kappa^1\text{:}\kappa^1\text{:}\eta^3\text{:}\eta^6\text{-}2,6\text{-}(2,6\text{-}i\text{-}Pr_2C_6H_3\text{-}N)_2\text{-}4\text{-}CH_3C_5H_2N)_2\}]$ (**17**).[27] It is worthy to note that the potassium cations are critical in the stabilization of **17**. Seemingly, the two pendant amido nitrogen atoms are stabilized by coordination to K^+ ions, so they do not coordinate to Cr centres and accordingly weaken the Cr-Cr quintuple bond. As a result, the yield of **17** dramatically increased from 6% to 82% with the presence of 5 equivalent of KI. It is also interesting to note that removal of one counter cation K^+ from **17** by adding 1 equivalent of 18-crown-6 ether caused the rupture of the Cr-Cr quintuple bond. Until that time, these reactions were unprecedented in the quintuple bonding system. Alternatively, when a solution of **58** in diethyl ether was treated with 2.5 equivalent of KC_8, **17** was obtained as well. In contrast, treatment of **59** or **61** in the presence of 5 equiv of KI with an excess amount of KC_8 doesn't show any sign of the analogous Cr-Cr quintuple bonded species. It is clear that the 2,6-i-$Pr_2C_6H_3$ groups play an important role in stabilizing the potassium cations through coordination.

((Scheme 11))

Characterization and Bonding

The type *II* configuration

The solid-state molecular structures of the quintuple bonded complexes **1-19** deciphered by X-ray crystallography gave a meticulous view about the skeletal geometry. As shown in Figure 3, the majority of these complexes are in the type *II* category. Compounds **1-4**[23,51] look like the theoretical type *I* compounds, but substantial interactions between two Cr centres and the *ipso* carbons of two flanking rings are present, so they are advertised a type *II* configuration. In addition to the type *II* configuration, the C_{2h} symmetry **1-4** display close agreement with DFT calculations, which predicted that the model compounds $(4\text{-}XC_6H_4)CrCr(C_6H_4\text{-}4\text{-}X)$ (X = H, $SiMe_3$, OMe and F) have similar geometries in the gas phase. The theoretical studies of **1** revealed that the Cr-Cr bonding is enhanced by the secondary interactions between Cr and the *ipso*-carbon of the flanking aryl rings, besides the intrinsic five bonding components of the Cr-Cr quintuple bond. Moreover, the presence of the *i*-Pr groups also provide further stabilization energy to **1** by about 20 kcal/mol relative to the two monomeric fragments Ar'Cr.[58, 59]

Furthermore, complexes **5** and **7-17** also come under the type *II* configuration. Comparisons between crystal structures of **7-10** (Figure 4) indicated that complexes **7-9** with two Cr and four N atoms being coplanar possess C_{2h} symmetry, while **10** exhibits a noncoplanar Cr_2N_4 core skeleton, which is a consequence of the inter-ligand steric repulsion between adjacent 2,6-i-$Pr_2C_6H_3$ substituents and the CH_3 groups of the ligand backbone.[25] In addition, the Cr-Cr quintuple bonded complex **17** shows the Cr_2 unit residing on the crystallographically imposed centre of symmetry of the type *II* configuration with C_{2h} symmetry as well.[37] Though the Cr-Cr quintuple bonds in **7**-**10** and **17** are supported by amidinates with different bulk and diamidopyridine, their Cr-Cr bond lengths are close to 1.74 Å.

((Fig. 4))

The most important metric parameter of quintuple bonded dinuclear complexes is by no means their metal-metal bond lengths.[60-62] The Cr-Cr bond length in **1** is 1.8351(4) Å and its effective bond order (EBO, from CASSCF/CASPT2 calculations, is defined as the sum of the occupation numbers of the bonding orbitals minus the corresponding sum for the antibonding orbitals divided by two)[63,64] is 3.43.[23] Though these values are not promising for a Cr-Cr quintuple bond, in light of the supershort Cr-Cr quadruple bond length of 1.828(2) Å in $Cr_2(2\text{-}MeO\text{-}5\text{-}MeC_6H_3)_4$,[65] the discovery of **1** initiated the quintuple bond length race. To study how the Cr-Cr quintuple bond length in **1** could be affected by the *para* substituent ($SiMe_3$, OMe, and F) on the central phenyl ring of the terphenyl ligand, Power et al. prepared three derivatives **2**-**4** (Figure 3) of **1**. Though compounds **2**-**4** showed significant variation on Cr-Cr distances ranging from 1.8077(7) to 1.8351(4) Å, it was attributed to the lattice packing, not associated with the electronic nature of the *para* groups.[51]

If electronic effect is not the situation, which factors will strongly influence the quintuple bond length? It is nothing but the ligand design**!** In the wake of Power's C-based terphenyl ligands, Theopold's quintuple bonded dichromium complex **5** supported by two N-based diazadiene ligands showed a Cr-Cr bond length of 1.8028(9) Å,[28] shorter than those of **1**-**4**.[51] Complexes **7**-**10** supported by the amidinato ligand with different substituents bulk displayed even shorter Cr-Cr bond lengths and higher natural bond orders (BO-NBO, from NBO analysis)[66-68] (**7**: 1.7404(8) Å and 4.27; **8**: 1.7454(1) Å and 4.25; **9**: 1.74729(10) Å and 4.26; **10**:1.7395(7) Å and 4.30).[25] The Cr-Cr bond length of the pyridylamide-stabilized **11** is 1.749(2) Å with a BO-NBO of 4.3.[29] Although the diamidopyridine-supported **17** is one of the type *II* compound, it is an unique compound, whereby the presence of two potassium counter-cations did not affect the Cr-Cr bond length of 1.7443(10) Å with a BO-NBO of 4.54.

The Cr-Cr bond length is influenced by ligands and this concept was recently demonstrated by Kempe et al. They utilized guanidinate ligands with different bulky backbones as a substitute for an amidopyridyl ligand and achieved the shortest Cr-Cr quintuple bonds in **15** and **16**, where the respective Cr-Cr bond length is 1.7293(12) and 1.7056(12) Å with a Wiberg bond index[69] of 4.43 (**15**)[35] and EBO of 3.93 (**16**).[36] There are many ways for describing the metal-metal multiple bond lengths. Comparing the bond distances in multiple bonds to the distances for single bonds is one of the best ways. The ratios of these values are called the formal shortness ratio (FSR).[2] Though the transition metals and main group elements are different in their size, only the small molecules, such as N_2 and alkynes, with FSR 0.786 of N≡N and 0.783 of C≡C triple bonds are relatively near to that of the metal-to-metal quintuple bonds in the quintuple bonded species. This comparison made easy understanding of the shortness of metal-metal separation in **7**-**10**, where the FSRs of all Cr-Cr bonds are comparable of 0.739 and that of **15** and **16** is 0.733 and 0.723, respectively. According to the theoretical calculations, the participation of the lone pair electrons of the nitrogen on the π systems of the bridging guanidinato ligand can give extra stability worth 17-27 kcal/mol to the Cr-Cr quintuple bond of **15**.[70]

To clarify that the thus far recognized Cr-Cr quintuple bonds are not a combination of covalent bonding with antiferromagnetic coupling, magnetic measurements on the quintuple bonded dichromium complexes **1**-**4**,[51] **12**[41] and **17**[34] show temperature-independent weak paramagnetism, consistent with strongly coupled d^5-d^5 bonding electrons. Furthermore, the Cr-Cr quintuple bonding was also corroborated by DFT calculations on **7** (Figure 5). The results indicated strong interactions between two d^5 Cr^I centres with five bonding orbitals (1σ, 2π and 2δ) occupied by five pairs of electrons. The HOMO-2 corresponds to the Cr-Cr σ bonding orbital (d_{z^2}+ d_{z^2}), and HOMO-3 (d_{xz}+d_{xz}) and HOMO-7 (d_{yz}+d_{yz}) exhibit the Cr-Cr dπ bonding interactions. Two Cr-Cr δ bonding orbitals are represented by HOMO (d_{xy}+d_{xy}) and HOMO-1. Of particular interest is that HOMO-1 is a side-on sd hybridized δ orbital (24.6% s and 75.4% $d_{x^2-y^2}$) aligned such that the main hybrid orbital axes are parallel to one another. No significant π interactions between Cr atoms and N donors are observed, which consequently result in two Cr-Cr δ bonding interactions in **7**.

((Fig. 5))

The quintuple bonded dichromium species characterized to date show that those N-donor-supported compounds have much shorter Cr-Cr bond lengths than those with C-donor ligands as indicated in Figure 3. The origin of this difference in Cr-Cr bond length is not clear. The ligand bridging effects may be the main cause. Tsai and Kempe reported that all bidentate three-atom bridging ligand-stabilized Cr-Cr quintuple bonds (**6**-**12** and **15**-**17**) show ultrashort Cr-Cr quintuple bonds, particularly, those carrying guanidinates **16** and **17**. On the other hand, when a four-atom bridging diazadienide was used as an ancillary ligand by Theoplod et al., a longer Cr-Cr quintuple bond length was observed in **5**. Interestingly, in Power's complexes **1**-**4**, the bulky terphenyl ligands also coordinate to the dichromium units in a bridging fashion, but much longer Cr-Cr bond lengths are observed. In light of the stronger σ donation of aryl ligands than amidinates, amidopyridines and a diazadienide, compounds **1**-**4** may have weaker Cr-Cr σ bonds than those of the N-donor stabilized quintuple bonded dichromium species.

In contrast to the large number of characterized quadruple bonded dimolybdenum complexes[2] and the predominating quintuple bonded dichromium complexes, there are only three quintuple bonded dimolybdenum complexes yet discovered. This could be blamed by the lack of suitable molybdenum precursors. The C_{2h} symmetry quintuple bonded dimolybdenum complexes **13** and **14** are the two remarkable examples of the type *II* configuration and their Mo-Mo distances are 2.0187(9) and 2.0157(4) Å, respectively, representing the shortest metal-metal bond lengths among the second row transition metals. These metric parameters revealed the fact that the steric bulkiness of the ancillary ligands has an insignificant influence on the Mo-Mo quintuple bond length. The other focal point is that the Mo-Mo bond lengths in **13** and **14** are substantially shorter than the theoretically predicted Mo-Mo quintuple bond lengths of 2.03-2.10 Å.[26] The FSR of the Mo-Mo quintuple bonds of **13** and **14** are 0.776 and 0.775, respectively.

The type *III* configuration

Out of the 19 structurally characterized quintuple bonded complexes, two of them are in the category of the type *III* configuration. The first type *III* complex **6** with D_3 symmetry discovered by Tsai and co-workers displayed each of both Cr atoms being unusual three-coordinate with respect to the ligands. In 2008, Tsai launched his studies in quintuple bonding by employing simple amidinato ligands to stabilize the unusual lantern type of Cr-Cr quintuple bonded species **6** with an ultrashort Cr-Cr bond length of 1.7397(9) Å with an MBO of 3.59.[24] It is noteworthy that the Cr-Cr quintuple bond length in **6** is shorter than those of the other C_{2h} 11 dichromium quintuple bonded complexes (**1-5**, **7-12** and **17**). In spite of the extremely short Cr-Cr bond, it is, at present, difficult to understand why **6** has a metal-metal quintuple bond, since the each Cr atom is ligated by three ligands, which is against the guideline of minimizing the coordination number of the metal centres to achieve a metal-metal quintuple bond. However, the conformation of **6** is consistent with Hoffmann's prediction on the D_{3h} quintuple bonded dinuclear species.[13] The crystal structure of **31**, the one-electron oxidized counterpart of **6**, exhibited C_{2v} symmetry, due to the unusual Jahn-Teller distortion in a dinuclear species. Such structure distortion arose from the uneven occupation of the two degenerate δ orbitals in the $\sigma^2\pi^4\delta^3$ electronic configuration of the Cr-Cr bonding. Just recently, Lu's group introduced another example of the type *III* heterodinuclear complex **19**, which is a diamangnetic complex with 3-fold symmetry having a short Mn-Cr quintuple bond of 1.8192(9) Å with EBO = 3.94.[30] It is worth pointing out that the quintuple bonded dichromium complexes usually show the metal-metal quintuple bond length less than 1.84 Å. Except **19**, all the other Mn-Cr heterodinuclear complexes having the metal-metal interactions are very weak with bond distances longer than 2.68 Å.[71,72]

The type *IV* Configuration

In 2012, Tsai and co-workers discovered the complex **17** showing the novel type *IV* conformation, which basically features a lantern structure and represents the only one example containing a hterotrinuclear triangular $LiMo_2$ unit. DFT calculations on the Li-spanned dimolybdenum trisamidiante complex **18** revealed the type *IV* quintuple bond with the Mo-Mo bond length of 2.0612(4) Å with a BO-NBO of 3.67, which is longer than those of **13** and **14**, but slightly shorter than the shortest Mo-Mo quadruple bond length of 2.063(1) Å in the tetrakisamidato dimolybdenum species $[Mo_2\{t\text{-BuNC(Me)O}\}_4]$.[73] The quintuple bonded Mo^{2+} moiety in **18** is electron rich, so it strongly binds a Li^+ cation, which spans the Mo-Mo quintuple bond with the Mo-Li bond order of 0.57.

Reactivity

As discussed earlier, the quintuple bonded complexes are expected to be highly reducing and kinetically reactive due to their low-valent and low-coordinate bimetallic units. Hence, the reactivity of these quintuple bonded dimers towards unsaturated organics and small inorganic molecules has recently been explored.

Reactions with small inorganic molecules

The reactivity study of quintuple bonded complexes was initiated by Power and Kempe. Upon introduction of N_2O to an *n*-hexane solution of **1**, the 76 kcal/mol worth strong Cr-Cr quintuple bond was cleaved completely. The reaction of **1** with N_2O yielded the dinuclear mixed-valent product $Ar'Cr(\mu\text{-}O)_2Cr(O)Ar'$ (**62**) through an oxygenation process (Scheme 12). Compound **62** contains two different Cr centres, which are bridged by two oxo groups, and one of them is terminally coordinated by one oxygen atom to result in the formation of Cr^{3+} and Cr^{5+} centres. The terminal Cr-O bond is shorter than the bridging Cr-O bond, an indication of a strong Cr=O double bond character.[37]

((Scheme 12))

Activation of group 15, 16 and 17 elements

Activation of some main group elements by the Cr-Cr quintuple bond was conducted by Kempe and co-workers by using their Cr-Cr quintuple bonded complex **12**. Reactions of **12** with group 15 elements, including P_4, AsP_3 and As_4, produced complexation products $[Cr(\mu\text{-}\kappa^2\text{-Ar})]_2[\mu_3\text{-}\kappa^1\text{-}\kappa^3\text{-}\kappa^3\text{-}E_4]$ (Ar = 2-(N-2,6-$Me_2C_6H_3$)-6-(2,6-*i*-$Pr_2C_6H_3$)C_5H_3N) (**63**: $E_4 = P_4$; **64**: $E_4 = As_4$; **65**: $E_4 = AsP_3$) with terminally bound *cyclo*-P_4^{2-}, *cyclo*-As_4^{2-}, and *cyclo*-AsP_3^{2-} units.[38] The Cr-Cr bond lengths in **63-65** are comparable at ca. 1.87 Å, which are longer than that in **12** by 0.12 Å, and is indicative of quadruple bonds. The formation of the square-planar P_4^{2-} and As_4^{2-} ligands along with the Cr-Cr quadruple bond in **63** and **64** are consistent with the oxidation of the quintuple bonded Cr_2 centre. On the other hand, the conformational deviation of the AsP_3 fragment in **65** from the square-planar geometry is presumably because of the size difference between phosphorus and arsenic atoms. These reactions represent for the first time the activation of group 15 elements in a one-step bimetallic fashion. Meanwhile, the *cyclo*-P_4 group in **63** was shown to display the capability of coordination to a single $W(CO)_5$ moiety and formed the heterotrimetallic complex $[Cr\text{-}(\mu\text{-}\kappa^2\text{-Ar})]_2[\mu_3\text{-}\kappa^1\text{-}\kappa^3\text{-}\kappa^3\text{-}P_4][W(CO)_5]$ (**66**). The bulky nature of **63** prevents the coordination of a second equivalent of $W(CO)_5$ fragment (Scheme 13).

As for the activation of group 16 elements, reactions of **12** with chalcogens, S_8, Se_8, and Te, yielded structurally similar bimetallic dichalcogenides $[Cr(\mu\text{-}\kappa^2\text{-Ar})]_2[\mu\text{-}\kappa^2\text{:}\kappa^2\text{-}E_2]$ (E = S (**67**), Se (**68**), Te (**69**)), which contain a distorted tetrahedral Cr_2E_2 central core and each chromium is in 2+ oxidation state.[40] Complexes **67**–**69** are diamagnetic and **67** has a shorter S-S bond length (2.058(4) Å) than expected for disulfur ligands.[74] The Cr-Cr bond lengths of **67** and **69** around 1.84 Å come in the quadruple bond category. Selective oxidation of the Cr-Cr quintuple bond of **12** with O_2 is a unique reaction due to the stronger oxidizing ability of O_2, compared to other heavier chalcogens and results in a diamagnetic dimeric oxo complex $[CrArO(\mu\text{-}O)]_2$ (**70**) with two bridged and two terminally coordinated oxo ligands and two pentavalent chromium ions.[39,41] This type of chromium oxo complexes is hardly observed and was first reported by Herberhold and co-workers.[75] The long Cr-Cr separation in **70** of 2.5314(10) Å is consistent with the single bond between the chromium atoms. In addition, the S-S and Se-Se bonds in diphenyldichalcogenides Ph_2S_2 and Ph_2Se_2 were also readily cleaved by **12** to give the isostructural dinuclear products $[Cr\text{-}(\mu\text{-}\kappa^2\text{-}Ar]_2[(\mu\text{-}EPh)_2]$ (E = S (**71**), Se (**72**)) by oxidative addition. Unlike the distorted tetrahedral Cr_2E_2 cores in **67**-**69**, the Cr_2E_2 cores in **71** and **72** adopt a butterfly geometry. The Cr-Cr separations in **71** and **72** of about (1.85 Å) are considered as supershort quadruple bonds (Scheme 13).

Compound **12** also undergoes facile halogenation. Reactions with halogens resulted in the formation of halogen-bridged dimeric complexes *trans*-$[Cr\text{-}(\mu\text{-}\kappa^2\text{-}Ar]_2[(\mu\text{-}X)_2]$ (X = Cl (**73**), Br (**74**), I (**75**)), where two halogen ligands bridge two Cr atoms in a *trans* fashion to give a diamond Cr_2X_2 core. Their Cr-Cr distances in the range of 1.86-1.92 Å lie in the range of known quadruple bonded complexes. As a result, the quintuple bonded dichromium complex can serve as a multi-electron (2-8) reductant when activated by small inorganic molecules (Scheme 13).

((Scheme 13))

Carboallumination reaction

Carboallumination reactions of carbon-carbon double and triple bonds have been thoroughly developed in the synthetic organic and organometallic chemistry.[76-78] "*Syn*-addition" for double bonds and "*cis* addition" for triple bonds are the key steps in carboallumination reactions. In 2009, Kempe et al. applied the carboallumination reaction to an inorganic molecule. They described a remarkable carboallumination reaction proceeding via the insertion of Cr-Cr quintuple bond in **12** into one of the Al-C bonds of $AlMe_3$ to give the diamagnetic carboallumination product *trans*-$[Cr_2(\mu\text{-}CH_3)(\mu\text{-}AlMe_2)(\mu\text{-}\kappa^2\text{-}Ar)_2]$ (**76**) with a bridging $AlMe_2$ and a Me ligand. The Cr-Cr bond length is 1.8365(8) Å, typical of a quadruple bond. This was further supported by the decrease in the Cr-Cr bond Wiberg index from 4.4 of **12** to 3.5 in **76**.[41] These results are consistent with the formal oxidative addition of an Al-C bond to the Cr-Cr quintuple bond, generating an anionic Al(I)Me_2 group. Theoretical calculations suggested charge transfer towards the Cr-Cr bond from the anionic $AlMe_2$ fragment. Of particular interest of **76** are the unusual long Cr-Al distances of ca. 2.90 Å (Scheme 14), compared with the regular coordination compounds containing direct Cr-Al bonds in the range of 2.38-2.48 Å.[79,80] The long Cr-Al separations were further supported by the calculated relative low Wiberg bond order of 0.30.[41] This type of reaction is a breakthrough in the quintuple bond chemistry, because it is disclosing strong parallels between the metal-metal quintuple bonds and C-C double and triple bonds.

((Scheme 14))

Nitric oxide activation

Nitric oxide disproportionation induced by mononuclear late divalent transition metal complexes (Mn, Fe, Ru, Co and Cu) has been well documented.[81-92] In 2013, Tsai and co-workers extended this field to the quintuple bonded dinuclear complexes. They succeeded in this type of reaction with both Cr and Mo quintuple bonded amidinate dimers.[40] As shown in Scheme 15, exposure of **8**, **9** and **14** to of NO yielded dichromium nitrosyl nitrito amidinato and quadruple bonded dimolybdenum amidinato nitrito species with interesting structure variety. The diamagnetic mononuclear complex $Cr(NO)_2[\kappa^2\text{-}HC(N\text{-}2,6\text{-}Et_2C_6H_3)_2]_2$ (**77**) and dinuclear species $Cr_2(\mu\text{-}\kappa^1\text{-}ONO)_2(NO)_4[\mu\text{-}\kappa^2\text{-}HC(N\text{-}2,6\text{-}Et_2C_6H_3)_2]_2$ (**78**) with a distorted octahedral geometry were the products from the reaction of **8** with an excess amount NO in toluene at −78 °C. It is noteworthy that at room temperature, **77** was the only identifiable product from the reaction of **8** with an excess amount of NO produced **77**, and **78** was not transferred to **77** upon heating. These observations imply the highly reactive nature of **8**, carrying two small amidinato ligands. Due to the bulky nature of its amidinate ligand, **9** reacted with NO to give the diamagnetic dinuclear complex $(\kappa^2\text{-}NO_2)Cr(\mu\text{-}NO)_2[\mu\text{-}\kappa^2\text{-}HC(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_2]_2CrNO$ (**79**). Compound **79** displayed an unsymmetrical configuration, in which two Cr atoms are spanned by two amidinates and two nitrosyls, and one Cr is ligated by an axial NO ligand, while the other is axially chelated by a nitrito group. It is interesting to note that the NO disproportionation proceeded in the axial position of one Cr atom in **79**. On the other hand, the reaction of **14** with NO in THF produced the paddlewheel complex *cis*-$Mo_2[\mu\text{-}\kappa^1\text{:}\kappa^1\text{-}NO_2]_2\text{-}[\mu\text{-}\kappa^2\text{-}PhC(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_2]_2$ (**80**). Though **80** features two bulky amidinate ligands, formed two nitrito ligands are arranged in a *cis* manner. An entirely different type of mechanism can be seen in **80** that the NO disproportionation takes place between two Mo atoms. The influence of axial coordination on the multiple bond strength was also observed in **78**-**80**. While **78** exhibits a long Cr-Cr distance of 3.081(1) Å and **79** has a Cr-Cr single bond (2.6252(12) Å), due to the lack of axial NO coordination in **80**, there is a strong interaction between Mo atoms consistent its bond length of 2.0857(4) Å, typical of a quadruple bond. These studies revealed some important findings: the Mo-Mo quintuple bond is much stronger than that of the analogous Cr-Cr quintuple bond, and the coordination mode and site of nitrito ligands to metals are strongly influenced by the metal centres and steric bulk of the supporting amidinato ligands.

((Scheme 15))

Reactions with organic functionalities

Quintuple bond destruction by 1-AdN_3 (Ad = adamantyl)

Not only can the Cr-Cr quintuple bond of **1** be readily ruptured by reacting with small inorganic N_2O,[37] O_2,[39, 40] and NO[40] as stated above, but it can also be destroyed by reacting with one equivalent of 1-AdN_3 and give the homodivalent complex $Ar'Cr(\mu_2\text{-}\kappa^1\text{:}\kappa^3\text{-}1\text{-}AdN_3)CrAr'$ (**81**) (Scheme 16). Within the bridging 1-AdN_3, the N-N distances of 1.330(5) and 1.304(5) Å and the N-N-N angle of 109.9(3)° render it a triazenido ligand.[37] It is noteworthy that two nitrogen coordinated chromium triazenido complexes are very rare. The complete cleavage of the Cr-Cr quintuple bond leading to **81** results from the insertion of an azido group into the Cr-Cr quintuple bond instead of the usual N_2 elimination. The three-coordinate chromium ion is ligated by two nitrogen atoms from the azido group and a terminal aryl group through the central *ipso* carbon and exists as distorted quasi T-shaped geometry.

((Scheme 16))

Cycloaddition reactions

Cycloaddition reactions of alkynes are a very useful protocol for the construction of a variety of hetero- and homocyclic aromatic molecules.[93-97] Besides alkynes, [2+2] and [2+2+2] cycloaddition reactions were recently found on group VI quintuple bonded complexes with unsaturated hydrocarbons.

Cycloaddition with unsaturated hydrocarbons

Kempe's group demonstrated cycloaddition reactions of the quintuple bonded chromium dimer with dienes.[42] Of the five bonding pairs of the Cr-Cr quintuple bond, one δ bond was involved in the reactions with the C-C double bonds of dienes. The reactions of **12** with 2-methyl-1,3-butadiene and 1,3-butadiene produced the cycloadducts $[Cr(\mu\text{-}Ar)]_2[\mu\text{-}\kappa^3\text{-}CH_2C(CH_3)CHCH_2]$ (**82**) and $[Cr(\mu\text{-}Ar)]_2[\mu\text{-}\kappa^3\text{-}CH_2CHCHCH_2]$ (**83**) (Ar = $[\{2\text{-}N(2,6\text{-}Me_2C_6H_3)\text{-}6\text{-}(2,6\text{-}i\text{-}Pr_2C_6H_3)\}C_5H_3N]$, respectively (Scheme 17A). Both structures of **82** and **83** are essentially similar. Both dienes coordinate to the Cr-Cr quintuple bond in their *cisoid* conformation and consequently push two aminopyridinato ligands bent away from the metal centres. Interestingly, in both **82** and **83**, the central C-C bond lengths are shorter than the terminal C-C bond lengths of the bound diene ligands, which suggest the central C-C linkages have a double bond character. Accordingly, this Deils-Alder-like addition of dienes to the Cr-Cr quintuple bond in **12** oxidised the monovalent chromium to divalent, and thus resulted in reduction of the Cr-Cr bond order, giving rise to the formation of quadruple bonded complexes **82** and **83** with Cr-Cr separations of ca. 1.82 Å.

[2+2] cycloaddition reactions

Kempe, Theopold, and Tsai reported [2+2] cycloaddition reactions of their quintuple bonded dimers with alkynes and the produced cycloadducts show good similarities in their structures. The quintuple bonded complexes **5**, **9**, **12** and **14** reacted with alkynes to yield the [2+2] cycloadducts $[Cr(\mu\text{-}Ar)]_2[(\mu\text{-}\kappa^2\text{-}RCCR')]$ (**84**: R = R' = C_6H_5; **85**: R = H, R' = C_6H_5; **86**: R = H, R' = $Si(CH_3)_3$; **87**: R = H, R' = $C_6H_4\text{-}p\text{-}CH_3$)[42] (Scheme 17 A), $[\mu\text{-}\kappa^2\text{-}(HCN\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_2Cr]_2(\mu\text{-}\kappa^2\text{-}RCCR)$ (**89**: R = Me; **90**: R = Et; **91**: R = Ph)[43] (Scheme 17B), $[Cr_2(\mu\text{-}\kappa^2\text{-}R^2\text{-}CCR^3)_2\{\mu\text{-}\kappa^2\text{-}HC\text{-}(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_2\}_2]$ (**92**: R^2 = H, R^3 = *n*-Pr; **93**: $R^2 = R^3$ = Et; **94**: $R^2 = R^3$ = Ph) (Scheme 18A), and $[Mo_2(\mu\text{-}\kappa^2\text{-}EtCCEt)_2\{\mu\text{-}\kappa^2\text{-}PhC(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_2\}_2]$ (**95**)[44] (Scheme 18 A), respectively. In cycloadducts **84-87** and **89-95**, the hydrogen atoms and the substituted groups of the bound alkynes bend back away from the metal centres, and this allows the π electron pair of the alkynes to bind efficiently to the metals. The hybridization of the alkyne carbon atoms consequently changes from sp to sp^2. As evidenced by NMR spectroscopy, the $N_{pyridine}$ and N_{amido} atoms of **84-85** are not exchanging their positions at room temperature due to the restricted rotation of the bulky 2,6-dialkylphenyl rings. The C_2Cr_2 cores in **84-87** and **89-95** are not planar and, in fact, the bridging alkyne ligands show a skewed arrangement with respect to the Cr-Cr quintuple bond axis due to a second order Jahn-Teller effect.[98,99] Noteworthy is that the twist angle in the skewed C_2Cr_2 arrangement increases with the steric hindrance of the alkyne substituents, presumably due to steric issues. Furthermore, the central C-C bond lengths of the coordinated alkynes in the X-ray structurally determined **87** and **89-95** elongated to the range of 1.315-1.356 Å, longer than the normal C-C triple bond (1.181 Å) and close to the C-C double bond (1.331 Å). On the other hand, elongation of the metal-metal distances was also observed in these complexes, and they are 1.8041(15) (**87**),[42] 1.9248(7) (**89**), 1.9361(7) (**90**), 1.9186(7) (**91**),[44] 2.0603(4) (**92**), 1.8054(6) (**93**), 1.7981(14) (**94**) and 1.8233(7) Å (**95**).[43] As a result, two-electron redox occurred between Cr_2^{2+} and Mo_2^{2+} units and alkynes in these complexes. All these metal-metal bonds fall in the quadruple bond category, although the Cr-Cr bond lengths are extremely short, but they are longer than the recently reported Cr-Cr quadruple bond (1.773(1) Å) in the guanidinate-supported dichromium compound $[Cr(Me)\{\mu\text{-}\kappa^2\text{-}(Me_3Si)_2NC(NCy)_2\}]_2$ (Cy = cyclohexyl).[100] In contrast, **5** reacted with the more electron deficient alkyne $F_3CC{\equiv}CCF_3$ to produce an unexpectedly diamagnetic species $Cr_2[\mu\text{-}\kappa^2\text{-}(HCN\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_2][\mu\text{-}\kappa^4\text{-}\{2,6\text{-}i\text{-}Pr_2C_6H_3NCH(CF_3CCCF_3)CH(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)\}]$ (**88**) instead of a [2+2] cycloadduct. In **88**, one α-diimine ligand and the alkyne were transformed into a localized iminoamide through a C-C coupling. Though the Cr-Cr bond length (1.9615(6) Å) of **88** is long, but still in the quadruple bond range. The dichotomy pathways of **5** with alkynes thus revealed that the HOMO of **5** has a ligand-based character. In contrast to the said cycloaddition reactions, the dimolybdenum compound **13** displayed a different pathway for the [2+2] addition reaction. Addition of 2 equiv of 3-hexyne to **13** yielded a diamagnetic double [2+2] cycloaddition product $Mo_2(H)(\mu\text{-}\kappa^2{:}\kappa^2\text{-}EtCCEt)_2[\kappa^2\text{-}HC(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_2][\kappa^3\text{-}HC(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)\text{-}(N\text{-}2\text{-}CH(CH_2)CH_3\text{-}6\text{-}i\text{-}PrC_6H_3)]$ (**96**) as shown in Scheme 18A. Two parallel alkynes in **96** coordinate to the Mo_2 unit in different hemispheres and are perpendicular to the Mo-Mo bond. Another interesting feature of **96** is the intramolecular sp^3 C-H oxidative addition of an amidinate ligand to two Mo atoms, resulting in the formation of a cyclometalated species, presumably, due to the bulky nature of the amidinato ligand. The Mo-Mo bond length of 2.4843(11) Å is in the double bond range,[2] and the averaged central C-C bond length of the bridging alkynes of about 1.32 Å is indicative of a double bond character. Such unique structure varieties made **96** different from other [2+2] cycloadducts **84-87** and **89-95**.

((Scheme 17))

((Scheme 18))

[2+2+2] cycloaddition reactions

Mononuclear metallabenzenes have been attention-catching complexes due to their ability to display aromatic properties. For the last 3 decades, the synthesis and reactivity studies of metallabenzenes have been developed based on the second and third row transition metals (Re, Ru, Os, Ir and Pt).[101-112] This field was recently extended to bimetallic systems by Tsai an co-workers on their discovery of the first two complexes containing a cyclically delocalized six membered C_4Mo_2 aromatic ring and the ring current involves δ electrons.[43] The remarkable bimetallic metallabenzenes $[Mo_2(\mu\text{-}\kappa^1{:}\kappa^1\text{-}1,3\text{-}n\text{-}Pr_2C_4H_2)\{RC(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_2\}_2]$ (**97**: R = H; **98**: R = Ph) were obtained from the reactions of **13** and **14** with two equivalent of terminal alkynes at room temperature through a head-to-tail C-C coupled [2+2+2] cycloaddition pathway. Remarkably, these two reactions are catalyst-free, which is in contrast with the [2+2+2] cycloaddition reactions of alkynes (Scheme 18B). No other regioisomers were observed in these two reactions. Complexes **97** and **98** show a lantern geometry, where two Mo atoms are three-coordinate with respect to the ligands. The most salient structural feature of **97** and **98** is that two *n*-Pr substituents of the C_4Mo_2 rings are on the same face of the six membered C_4Mo_2 ring. The Mo-Mo distances of **97** and **98** of about 2.14 Å are comparable to that of the paddlewheel complexes having Mo-Mo bond order 3.5.[113-119] The electronic delocalization in the metallacycles of **97** and **98** was revealed by theoretical calculations. The ring current was composed of a six-electron six-centre π-δ conjugation system. The electronic contributors to the C_4Mo_2 ring are 1,3-butadienyl fragment (4 π electrons) and Mo-Mo δ (d_{xy}-d_{xy}) (2 electrons) bond. Moreover, the P_π(C))-d_δ(Mo) π conjugation within the C_4Mo_2 ring was evidenced by the smaller Mo-Mo BO-NBO of 2.66. Compounds **97** and **98** can be thought as produced from an edge substitution of a multiple bonded M_2 unit for a C_2 unit in a benzene molecule. Furthermore, they represent the first metallabenzenes, which contain a multiple bonded dimolybdenum fragment. In view of the [2+2] cyclodadducts **84-87** and **89-95**, the formation of **97** and **98** is very likely via the [2+2] cycloadducts $[Mo_2(\mu\text{-}\kappa^2\text{-}n\text{-}PrCCH)\{\mu\text{-}\kappa^2\text{-}RC(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_2\}_2]$ (**99**: R = H; **100**: R = Ph). One of the surprising properties of **97** is its ability to catalyze the cyclotrimerization of 1-pentyne to give 1,3,5-tripropylbenzene at ambient temperature.

Friedel-Crafts-type haloacylation

After the successful achievement of [2+2+2] cycloaddition reactions of the Mo-Mo quintuple bond with terminal alkynes, Tsai accomplished the first example of Friedel-Crafts-type haloacylation of metal-metal quintuple bonded complexes. In the absence of catalysts, **9** and **13** reacted with acyl halides RCOX (R = C_6H_5, 2-MeC_6H_4, Me; X = Cl, Br) to produce β-halo α,β-quadruple bonded dimolybdenum acyl complexes, $[Cr_2(\mu\text{-}Cl)(\mu\text{-}\kappa^2\text{-}OC\text{-}2\text{-}MeC_6H_4)\{\mu\text{-}\kappa^2\text{-}HC(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_2\}_2]$ (**101**) $[Mo_2(X)(\mu\text{-}\kappa^2\text{-}OCR)\{\mu\text{-}\kappa^2\text{-}HC(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_2\}_2]$ (**102**: X = Cl, R = C_6H_5; **103**: X = Br, R = C_6H_5; **104**: X = Cl, R = 2-MeC_6H_4; **105**: X = Cl, R = CH_3) as displayed in Scheme 19.[45] In contrast with the stability of **102-105**, **101** quickly decomposes in THF. Both **102** and **103** show a *trans-cis*oid configuration, whereas *trans* β-chloro vinyl ketones usually display a *trans-trans*oid conformation. The Mo-Mo bond length in **102** and **103** (ca. 2.08 Å) is within the range of a typical quadruple bond. Interestingly, the β-halo α,β-quadruple bonded dimolybdenum acyl complexes can further react with another equivalent of acyl halides to give alkylidyne complexes via acyl disproportionation. That is, **102-105** further reacted with another equivalent of acyl halides to yield $[Mo_2(X)(\mu\text{-}X)(\mu\text{-}CR)(\kappa^2\text{-}O_2CR)\{\mu\text{-}\kappa^2\text{-}HC(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_2\}_2]$ (**106**: Ar = C_6H_5, X = Cl; **107**: Ar = C_6H_5, X = Br; **108**: Ar = 2-MeC_6H_4, X = Cl; **109**: R = CH_3, X = Cl). Mechanistically, the alkylidyne groups in **106-109** were resulted from the first equivalent of acyl halides and the carboxylate ligands were derived from the second acyl halides via oxo transfer between two acyl groups, which was supported by the characterization of two arylidyne isomers, namely, $[Mo_2(Cl)(\mu\text{-}Cl)(\mu\text{-}CC_6H_5)(\kappa^2\text{-}O_2C\text{-}2\text{-}MeC_6H_4)\{\mu\text{-}\kappa^2\text{-}HC(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_2\}_2]$ (**110**) and $[Mo_2(Cl)(\mu\text{-}Cl)(\mu\text{-}C\text{-}2MeC_6H_4)(\kappa^2\text{-}O_2CC_6H_5)\{\mu\text{-}\kappa^2\text{-}HC(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_2\}_2]$ (**111**). Compound **110** was obtained by the addition of one equiv of o-toluoyl chloride to **102**, while **111** was isolated by mixing **104** and one equiv of benzoyl chloride. Surprisingly, **101** did not show any reactivity towards acyl halides, presumably, due to the less enolate character of the chromium acyl group and less reducing divalent chromium centres. Complexes **106**, **107**, and **109-111** show remarkably shorter Mo-Mo double bonds (2.43-2.48 Å) than the reported Mo-Mo double bond lengths within the range 2.58 to 2.62 Å.[120] Another intriguing finding on the alkynlidyne species **106-111** is that the halo ligands are labile, which readily undergo intra- and intermolecular halo exchange reactions. The lability of the halo ligands is likely due to the strong *trans*-effect alkylidyne groups.

The recognition of the [2+2] cycloadducts **84-87** and **89-95** (mainly dichromium) and [2+2+2] products **97** and **98** suggest the Mo-Mo quintuple bond is more reactive towards alkynes than the analogous Cr-Cr quintuple bond, presumably due to the higher Mo-C bond strength. Moreover, the facile haloacylation of **9** and **13** to give the metal-to-metal quadruple bonded **101-105** indicates a strong similarity between the metal-metal δ bond and the C-C π bond. As a result, the sufficient reactivity of the group 6 metal-metal quintuple bonded complexes are expected to give a wide platform for various reactivities as in unsaturated hydrocarbons.

((Scheme 19))

Conclusions and Outlook

The concept of metal-to-metal quintuple bonding originated from theoretically well explained *trans*-bent dinuclear transition metal complexes. In contrast with the theoretical *trans*-bent complexes, three different types (*II-IV)* of quintuple bonded dimers have been discovered and they all feature sterically encumbered ligands. Metal-ligand bond flexibility plays a vital role in the stabilization of the metal-metal quintuple bond. That is, the bulky ligand components should be spatially arranged in such a way that the metal-metal separation might be under control. The metal-N bonds are flexible enough to tune the steric hindrance of the supporting ligands, and, consequently, all the quintuple bonded complexes after Power's quintuple bonded Cr-dimer, are stabilized by N-based ligands (guanidinate, amidinate, amidopyridine). In view of the soft nature of the univalent metals in the quintuple bonded species, a soft phosphorus-based ligand is expected to show higher affinity towards these low-valent metal atoms. This was recently encouraged by the characterization of the heterodinuclear quintuple bonded Cr-Mn compound **19** stabilized by an N-P hybrid ligand. Hence, the chance to synthesize the metal-to-metal quintuple bonded complexes has increased by the utilization of other donors, such as O, S and mixed N-O, N-S, P-O and P-S donor ligands with appropriate substituents. In short, a judicious choice of ligand is the key in the preparation of the quintuple bonded complexes

The metal-metal bond length is the most interesting metric parameter in the quintuple bonded complexes, and it is mainly affected by the ancillary ligands. For example, by comparing **1**, **7-10**, **16** and **19**, whose metal-metal lengths are in the range of

1.70-1.84 Å, we immediately know the metal-metal quintuple bond lengths are associated with the ligands with different donor atoms and bulk. The longest metal-metal bond length comes with the strongest σ-donor ligand in **1**, and the shortest metal-metal quintuple bond length is accompanied by the most sterically hindered ligand in **16**. On the other hand, the metal-metal quintuple bond lengths may not be dependent on the geometry of the complexes. For example, ultrashort metal-metal quintuple bond lengths were observed in **6** and **19**, stabilized by three amidinate ligands and the double decker ligand N(o-(*i*-$Pr_2PCH_2N)C_6H_4)_3$ with three bridging arms, respectively. As a result, the C_3-symmetric quintuple bonded bimetallic complexes remain largely unexplored and future studies promise a better understanding of their structure and metal-metal bond length relationship. For Mo-Mo quintuple bonds, such analysis is thus far not possible as the number of characterized structures is relatively small, compared with the large number of quadruple bonded dimolybdenum complexes.

The low-valent and low-coordinate quintutple bonded species were shown to activate small inorganic molecules through reductive cleavage, complexation, and disproportionation pathways. Conversion of these small molecules into more economically useful materials by the quintuple bonded compounds is accordingly highly anticipated. More interestingly, quintuple bonded complexes were also shown to behave like unsaturated organic moieties in terms of their reactivity, such as cycloaddition, carbometallation, and haloacylation. These analogies effectively bridge inorganic and organic chemistry. Therefore, derivatization of metal-metal quintuple bonded complexes is worthy to explore.

Up to now, the quintuple bonded dinuclear species have been mainly focused on the group VI elements. Identification of compounds containing quintuple bonded bimetallic units will definitely help chemists gain more insight into this field. Accordingly, tungsten,[121] the heavier congener of Cr and Mo, has been the next possible candidate. In addition, theoretical studies by Gagliardi revealed that uranium[122,123] and protactinium[123] can also form metal-metal quintuple bonds in simple diatomic molecules. King et al. also suggested that tungsten,[121] osmium[123,125] and rhenium[121,124] in the hypothetic molecules Cp_2M_2 could possibly form metal-metal quintuple bonds. Attention should be paid to niobium as well, since the Nb_2 molecule has been experimentally probed and predicted to have a strong quintuple bond,[12] consistent with the electronic configuration $4d^45s^1$ of Nb atom. King's theoretical studies revealed that $Nb_2(CO)_8$ should have a Nb-Nb quintuple bond.[125] Though it will be challenging for the characterization of U_2, Pa_2 and Nb_2, a synthetic strategy similar to the identification of the bulky neutral N-heterocyclic carbine-stabilized diboryne[126] may be applied in this regard.

Acknowledgements

The authors are indebted to National Science Council (Grants NSC 99-2113-M-007-012-MY3) of Taiwan and Frontier Research Centre on Fundamental and Applied Sciences of Matters of National Tsing Hua University for financial support.

Notes and references

Department of Chemistry and Frontier Research Centre on Fundamental and Applied Sciences of Matters, National Tsing Hua University, Hsinchu 30013, Taiwan. Fax: 886-3-5711082; Tel: 886-3-5718232; E-mail: yictsai@mx.nthu.edu.tw.

1 G. N. Lewis, *J. Am. Chem. Soc.*, 1916, **38**,762; *Valence and the Structure of Atoms and Molecules*, Chemical Catalogue Co., New York, 1923.

2 F. A. Cotton, C. A. Murillo and R. A. Walton, *Multiple Bond Between Metal Atoms*, Springer, Berlin,3rd Ed.

3 F. A. Cotton, M. F. Curtis, C. B. Harris, B. F. G. Johnson, S. J. Lippard, J. T. Mague, W. R. Robinson and J. W. Wood, *Science* 1964, **145**, 1305.

4 B. O. Roos, A. C. Borin and L. Gagliardi, *Angew. Chem. Int. Ed.* 2007, **46**, 1469.

5 E. P. Kundig, M. Moskovits and G. A. Ozin, *Nature* 1975, **254**, 503.

6 M. H. Chisholm and A.M. Macintosh, *Chem. Rev.* 2005, **105**, 2949.

7 A. Kant and B. Strauss, *J. Phys. Chem.* 1966, **45**, 3161.

8 Z. L. Xiao, R. H. Hauge and J. L. Margrave, *J. Phys. Chem.* 1992, **96**, 636.

9 M. D. Morse, *Chem. Rev.* 1986, **86**, 1049.

10 Casey and D. G. Leopold, *Chem. Phys. Lett*. 1993, **97**, 816.

11 S. K. Gupta, R. H. Atkins and J. L. Margrave, *J. Phys. Chem. Commn.* 1992, **96**, 636.

12 W. Klotzbucher and G. A. Ozin, *Inorg. Chem*. 1977, **16**, 984.

13 A. Dedieu, T. A. Albright and R. Hoffmann, *J. Am. Chem. Soc.* 1979, **101**, 3141.

14 F. Weinhold and C. R. Landis, *Chem. Ed. Res. Pract. Eur*. 2001, **2**, 91.

15 F. Weinhold and C. R. Landis, *Valency and Bonding. A Natural Bond Orbital Donor-Acceptor Perspective*, Cambridge Uviversity Press: Cambridge, Uk/New York, 2005, p. 555.

16 C. R. Landis and F. Weinhold, *J. Am. Chem. Soc*. 2006, **128**, 7335.

17 F. Weinhold and C. R. Landis, *Science* 2007, **316**, 61.

18 L. Gagliardi, B. O. Roos, *Lect. Ser. Comput. Sci*. 2006, **6**.

19 M. Brynda, L. Gagliardi, P. O. Widmark, P. P. Power and B. O. Roos, *Angew. Chem. Int. Ed.* 2006, **118**, 3888.

20 B. O. Roos, A. C. Borin and L. Gagliadi, *Angew. Chem. Int. Ed.* 2007, **119**, 1493.

21 M. Brynda, L. Gagliardi, B. O. Roos, *Chem. Phys. Lett*. 2009, **471**, 1.

22 G. Merino, K. J. Donald, J. S. D. Acchidi and R. Hoffmann, *J. Am. Chem. Soc.* 2007, **129**, 15295.

23 T. Nguyen, A. D. Sutton, S. Brynda, J. C. Fettinger, G. J. Long and P. P. Power, *Science* 2005, **310**, 844.

24 Y.-C. Tsai, C.-W. Hsu, J.-S. K. Yu, G.-H. Lee, Y. Wang and T.-S Kuo, *Angew. Chem. Int. Ed*. 2008, **47**, 7250.

25 C.-W. Hsu, J.-S. K. Yu, C.-H. Yen, G.-H. Lee, Y. Wang and Y.-C. Tsai, *Angew. Chem. Int. Ed*. 2008, **47**, 9933.

26 Y.-C. Tsai, H.-Z. Chen, C.-C. Chang, J.-S. K. Yu, G.-H. Lee, Y. Wang and T.-S. Kuo, *J. Am. Chem. Soc*. 2009, **131**, 12534.

27 Y-L. Huang, D-Y. Lu, H-C. Yu, J-S. K. Yu, C-W. Hsu, T-S. Kuo, G-H. Lee, Y. Wang and Y-C. Tsai, *Angew. Chem. Int. Ed*. 2012, **51**, 7781.

28 K. A. Kreisel, G. P. A. Yap, P. O. Dmitrenko, C. R. Landis and K. H. Theopold, *J. Am. Chem. Soc*. 2007, **129**, 14162.

29 A. Noor, F. R. Wagner and R. Kempe, *Angew. Chem. Int. Ed.* 2008, **47**, 7246.

30 L. J. Clouston, R. B. Siedschlag, P. A. Rudd, N. Planas, S. Hu, A. D. Miller, L. Gagliardi and C. C. Lu, *J. Am. Chem. Soc*. 2013, **135**, 13142.

31 N. V. S. Harisomayajula, A. K. Nair, and Y.-C. Tsai, *Chem. Commun*. 2014, DOI:10.1039/C3CC48203K.

32 S.-A. Hua, Y.-C. Tsai and S.-M. Peng, *J. Chin. Chem. Soc*. 2014, **61**, 9.

33 S.-C. Liu, W.-L. Ke, J.-S. K. Yu, T.-S. Kuo and Y.-C. Tsai, *Angew. Chem. Int. Ed*. 2012, **51**, 6394.

34 Y.-L. Huang, D.-Y. Lu, H.-C. Yu, J.-S. K. Yu, C.-W. Hsu, T.-S. Kuo, G.-H. Lee, Y. Wang and Y.-C. Tsai, *Angew. Chem. Int. Ed*. 2012, **51**, 7607.

35 A. Noor, G. Glatz, R. Müller, M. Kaupp, S. Demeshko and R. Kempe, *Z. Anorg. Allg. Chem*. 2009, **635**, 1149.

36 A. Noor, T. Bauer, T. K. Todorova, B. Weber, L. Gagliardi and R. Kempe, *Chem. Eur. J*. 2013, **19**, 9825.

37 C. Ni, B. D. Ellis, G. J. Long and P. P. Power, *Chem. Commun*. 2009, 2332.

38 C. Schwarzmaier, A. Noor, G. Glatz, M. Zabel, A. Y. Timoshkin, B. M. Cossairt, C. C. Cummins, R. Kempe and M. Scheer, *Angew. Chem. Int. Ed*. 2011, **50**, 7283.

39 E. S. Tamne, A. Noor, S. Qayyum, T. Bauer and R. Kempe, *Inorg. Chem*. 2013, **52**, 329.

40 P.-F. Wu, S.-C. Liu, Y.-J. Shieh, T.-S. Kuo, G.-H. Lee, Y. Wang and Y.-C. Tsai, *Chem. Commun*. 2013, **49**, 4391.

41 A. Noor, G. Glatz, R. Muller, M. Kaupp, S. Domeshko and R. Kempe, *Nat. Chem*. 2009, **1**, 322.

42 A. Noor, E. S. Tamne, S. Qayyum, T. Bauer and R. Kempe, *Chem. Eur. J*. 2011, **17**, 6900.

43 H.-Z. Chen, S.-C. Liu, C.-H. Yen, J.-S. K. Yu, Y.-J. Shieh, T.-S. Kuo and Y.-C. Tsai, *Angew. Chem. Int. Ed*. 2012, **51**, 10342.

44 J. Shen, G. P. A. Yap, J. P. Werner and K. H. Theopold, *Chem. Commun*. 2011, **47**, 12191.

45 H.-G. Chen, H.-W. Hsueh, T.-S. Kuo and Y.-C. Tsai, *Angew. Chem. Int. Ed*. 2013, **52**, 10256.

46 R. Ponec and F. Feixas, *J. Phys. Chem. A*. 2009, **113**, 8394.

47 Y. I. Kurokawa, Y. Nakao and S. Sakaki, *J. Phys. Chem. A*. 2009, **113**, 3202.

48 L.-C. Wu, C.-W. Hsu, Y.-C. Chuang, G.-H. Lee, Y.-C. Tsai and Y. Wang, *J. Phys. Chem. A* 2011, **115**, 12602.

49 A. Wurtz. *Annalen der Chemie and Pharmacie.* 1855, **96**, 364.

50 A. D. Sutton, T. Ngyuen, J. C. Fettinger, M. M. Olmstead, G. J. Long and P. P. Power, *Inorg. Chem*. 2007, **46**, 4809.

51 R. Wolf, C. Ni, T. Nguyen, M. Brynda, G. J. Long, A. D. Sutton, R. C. Fischer, J. C. Fettinger, M. Hellman, L. Pu and P. P. Power, *Inorg. Chem*. 2007, **46**, 11277.

52 F. A. Cotton, L. M. Daniels, C. A. Murillo and P. Schooler, *J. Chem. Soc., Dalton Trans*. 2000, 2007.

53 M. Carrasco, N. Carado, C. Maya, R. Peloso, A. Rodriguez, E. Ruiz, S. Alvarez and E. Carmona, *Angew. Chem. Int. Ed*. 2013, **52**, 3227.

54 F. A. Cotton and D. J. Timmons, *Polyhedron,* 1998, **17**, 179.

55 P. A. Rudd, S. Liu, N. Planas, E. Bill, L. Gagliardi and C. C. Lu, *Angew. Chem. Int. Ed*. 2013, **52**, 4449.

56 P. A. Rudd, S. Liu, L. Gagliardi, V. G. Young and C. C. Lu, *J. Am. Chem. Soc*. 2011, **133**, 20724.

57 R. Wolf, M. Brynda, C. Ni, G. J. Long and P. P. Power, *J. Am. Chem. Soc*. 2007, **129**, 6076.

58 S. Ndambuki and T. Ziegler, *Inorg. Chem*. 2012, **51**, 7794.

59 G. L. Macchia, L. Gagliardi, P. P. Power and M. Brynda, *J. Am. Chem. Soc*. 2008, **130**, 5104.

60 G. L. Manni, A. L. Dzubak, A. Mulla, D. W. Brogden, J. F. Berry and L. Gagliardi, *Chem. Eur. J*. 2012, **18**, 1737.

61 G. L. Macchia, G. L. Manni, T. K. Todorova, M. Brynda, F. Aquilante, B. O. Roos and L. Gagliardi, *Inorg. Chem*. 2010, **49**, 5216.

62 G. L. Macchia, F. Aquilante, V. Veryazov, B. O. Roos and L. Gagliardi, *Inorg. Chem*. 2008, **47,** 11455.

63 B. O. Roos, *Adv. Chem. Phys*. 1987, p.399.

64 M. Brynda, L. Gagliardi, P. O. Power and B. O. Roos, *Angew. Chem. Int. Ed*. 2006, **45**, 3804.

65 F. A. Cotton, S. A. Koch and M. Miller, *Inorg. Chem*. 1978, **17**, 2084.

66 A. E. Reed, L. A. Curtiss and F. Weinhold, *Chem. Rev*. 1988, **88**, 899.

67 A. E. Reed, F. Weinhold, L. A. Curtiss and D. J. Pochatko, *J. Chem. Phys*. 1986, **84**, 5687.

68 J. E. Carpenter and F. Weinhold, *J. Am. Chem. Soc*. 1988, **110**, 368.

69 K. B. Wiberg, *Tetrahedron* 1968, **24,** 1083.

70 S. Ndambuki and T. Ziegler, *Inorg. Chem*. 2013, **52**, 3860.

71 F. Allen, *Acta Crystallogr., Sect. B* 2002, **58**, 380.

72 Y. Turov and J. F. Berry, *Dalton Trans*. 2012, **41**, 8153.

73 D. L. Lichtenberger, J. G. Kristofzski, and M. A. Bruck, *Acta Crystallogr. C* 1988, **44**, 1523.

74 A. Muller and W. Jaegermann, *Inorg. Chem,* 1979, **18**,2631.

75 M. Herberhold, W. Kremnitz, A. Razavi, H. Schollhorn and U. Thewalt, *Angew. Chem*. 1985, **97**, 603; *Angew. Chem. Int. Ed*. 1985, **24**, 601.

76 E. Shirakawa, T. Yamagami, T. Kimura, S. Yamaguchi and T. Hayashi, *J. Am. Chem. Soc*. 2005, **127**, 17164.

77 N. F. McKineley and D. F. O'Shea, *J. Org. Chem*. 2006, **71**, 9552.

78 S. Nakamura and M. Uchiyama, *J. Am. Chem. Soc*. 2007, **129**, 28.

79 Q. Yu, A. Purath, A. Donchev and H. Schnöckel, *J. Orgnomet. Chem*. 1999, **584**, 94.

80 H. Fölsing, O. Segnitz, U. Bossek, K. Merz, M. Winter and R. A. Fischer, *J. Organomet. Chem*. 2000, **606**, 132.

81 K. J. Franz and S. J. Lippard, *J. Am. Chem. Soc*., 1998, **120**, 9034.

82 K. J. Franz and S, J. Lippard, *J. Am. Chem. Soc*. 1999, **121**, 10504.

83 T. Yoshimura, *Inorg. Chim. Acta* 1984, **83**, 17.

84 I. M. Lorkovic and P. C. Ford, *Inorg. Chem*. 1999, **38**, 1467.

85 K. M. Miranda, X. Bu, I. M. Lorkovic and P. C. Ford, *Inorg. Chem*. 1997, **36**, 4383.

86 J. Kozhukh and S. J. Lippard, *J. Am. Chem. Soc*. 2012, **134**, 11120.

87 K. J. Franz, L. H. Doerrer, B. S. Spingler and J. Lippard, *Inorg. Chem*. 2001, **40**, 3774.

88 D. Gwost and K. G. Caulton, *Inorg. Chem*. 1974, **13**, 414.

89 P. Gans, *J. Chem. Soc. A*. 1967, 943.

90 J. L. Schneider, S. M. Carrier, C. E. Ruggiero, V. G. Young Jr. and W. B. Tolman, *J. Am. Chem. Soc*. 1998, **120**, 11408.

91 P. P. Paul and K. D. Karlin, *J. Am. Chem. Soc*. 1991, **113**, 6331.

92 C. E. Ruggiero, S. M. Carrier and W. B. Tolman, *Angew. Chem. Int. Ed. Engl.* 1994, **33**, 895.

93 G. Domínguez and Pérez-Castells, *J. Chem. Soc. Rev*. 2011, **40**, 3430.

94 D. Leboeuf, V. Gandon and M. Malacria in *Handbook of Cyclization Reactions*, Vol. 1 (Ed.: S. Ma), Wiley-VCH, Weinheim, 2009, pp. 367.

95 P. C. Chopade and J. Louie, *Adv. Synth. Catal*. 2006, **348**, 2307.

96 S. Kotha, E. Brahmachary and K. Lahiri, *Eur. J. Org. Chem*. 2005, 4741 .

97 J. A. Varela, C. Saá, *Chem. Rev*. 2003, **103**, 3787.

98 M. J. Calhorda and R. Hoffmann, *Organometallics*, 1986, **5**, 2181.

99 M. H. Chisholm and M. A. Lynn, *J. Orgnomet. Chem*. 1998, **550**, 141.

100 S. Horvath, S. I. Gorelsky, S. Gambarotta, I. Korobkov, *Angew. Chem. Int. Ed*. 2008, **47**, 9937.

101 D. L. Thorn and R. Hoffmann, *Nouv. J. Chim*. 1979, **3**, 39.
102 G. P. Elliott, W. R. Roper and J. M. Waters, *J. Chem. Soc. Chem. Commun*. 1982, 811.
103 H. Xia, G. He, H. Zhang, T. B. Wen, H. H. Y. Sung, I. D. Williams and G. Jia, *J. Am. Chem. Soc*. 2004, **126**, 6862.
104 P. Barrio, M. A. Esteruelas and E. Oñate, *J. Am. Chem. Soc*. 2004, **126**, 1946.
105 J. R. Bleeke, Y. F. Xie, W. J. Peng and M. Chiang, *J. Am. Chem. Soc*. 1989, **111**, 4118.
106 R. D. Gilbertson, T. J. R. Weakley and M. M. Haley, *J. Am. Chem. Soc*. 1999, **121**, 2597.
107 M. Paneque, C. M. Posadas, M. L. Poveda, N. Rendón, V. Salazar, E. Oñate and K. J. Mereiter, *J. Am. Chem. Soc*. 2003, **125**, 9898.
108 G. R. Clark, G. Lu, W. R. Roper and L. J. Wright, *Organometallics*. 2007, **26**, 2167.
109 V. Jacob, T. J. R. Weakley and M. M. Haley, *Angew. Chem. Int. Ed*. 2002, **41**, 3470.
110 H. Zhang, H. Xia, G. He, T. B. Wen, L. Gong and G. Jia, *Angew. Chem. Int. Ed*. 2006, **45**, 2920.
111 H. Zhang, L. Feng, L. Gong, L. Wu, G. He, T. B. Wen, F. Yang and H. Xia, *Organometallics***.** 2007, **26**, 2705.
112 G. R. Clark, T. R. O'Neale, W. R. Roper, D. M. Tonei, and L. J. Wright, *Organometallics*. 2009, **28**, 567.
113 F. A. Cotton, B. A. Frenz and T. R. Webb, *J. Am. Chem. Soc*. 1973, **95**, 4431.
114 P. J. Bailey, S. F. Bones, L. A. Mitchel, S. Parsons, K. J. Taylor and L. J. Yellowless, *Inorg. Chem*. 1997, **36**, 867.
115 P. J. Bailey, S. F. Bones, L. A. Mitchel, S. Parsons, K. J. Taylor and L. J. Yellowless, *Inorg. Chem*.1997, **36**, 5420.
116 F. A. Cotton, L. M. Daniels, E. A. Hillard and C. A. Murillo, *Inorg. Chem*. 2002, **41**, 1639.
117 F. A. Cotton, L. M. Daniels, C. A. Murillo, D. J. Timmons and C. C. Wilkinson, *J. Am. Chem. Soc*. 2002, **124**, 9249.
118 W. Fang, Q. He, Z. F. Tan, C. Y. Liu, X. Lu and C. A. Murillo, *Chem. Eur. J*. 2011, **17**, 10288.
119 Z. F. Tan, C. Y. Liu, Z. Li, M. Meng and N. S. Weng, *Inorg. Chem*. 2012, **51**, 2212.
120 M. D. Curtis, *Polyhedron* 1987, **6**, 759.
121 B. Xu, Q. S. Li, Y. Xie, R. B. King and H. F. Schaefer III, *J. Chem. Theory Comput*. 2010, **6**, 735.
122 L. Gagliardi and B. O. Roos, *Nature.* **2005**, 433, 848.
123 B. O. Roos, P. A. Malmqvist and L. Gagliaradi, *J. Am. Chem. Soc*. 2006, **128**, 17000.
124 B. Xu, Q. S. Li, Y. Xie. R. B. King and H. F. Schaefer III, *J. Phys. Chem. A*. 2009, **113**, 12470.
125 L. Tang, Q. Luo, Q. S. Li, Y. Xie, R. B. King and H. F. Schaefer III, *J. Chem. Theory Comput*. 2012, **8**, 862.
126 H. Braunschweig, R. D. Dewhurst, K. Hammond, J. Mies, K. Radacki and A. Vargas, *Science* 2012, **336**, 1420.

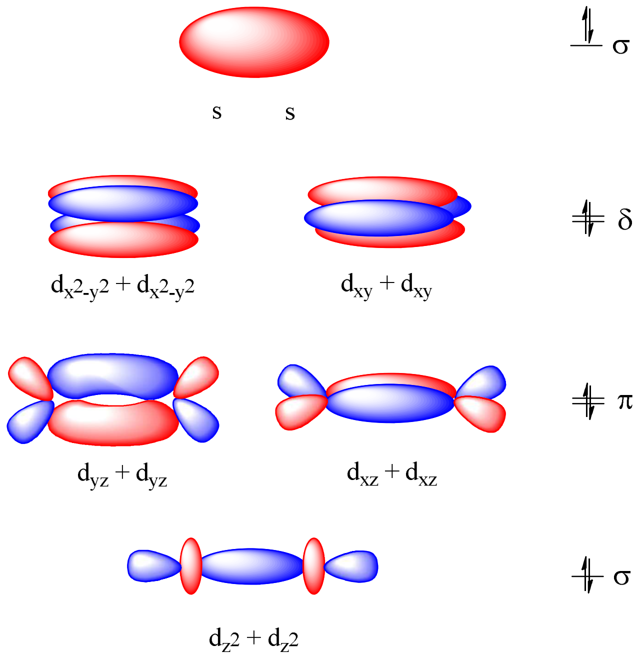


Figure 1. The bonding molecular orbitals of the group VI diatomic M_2 molecules.

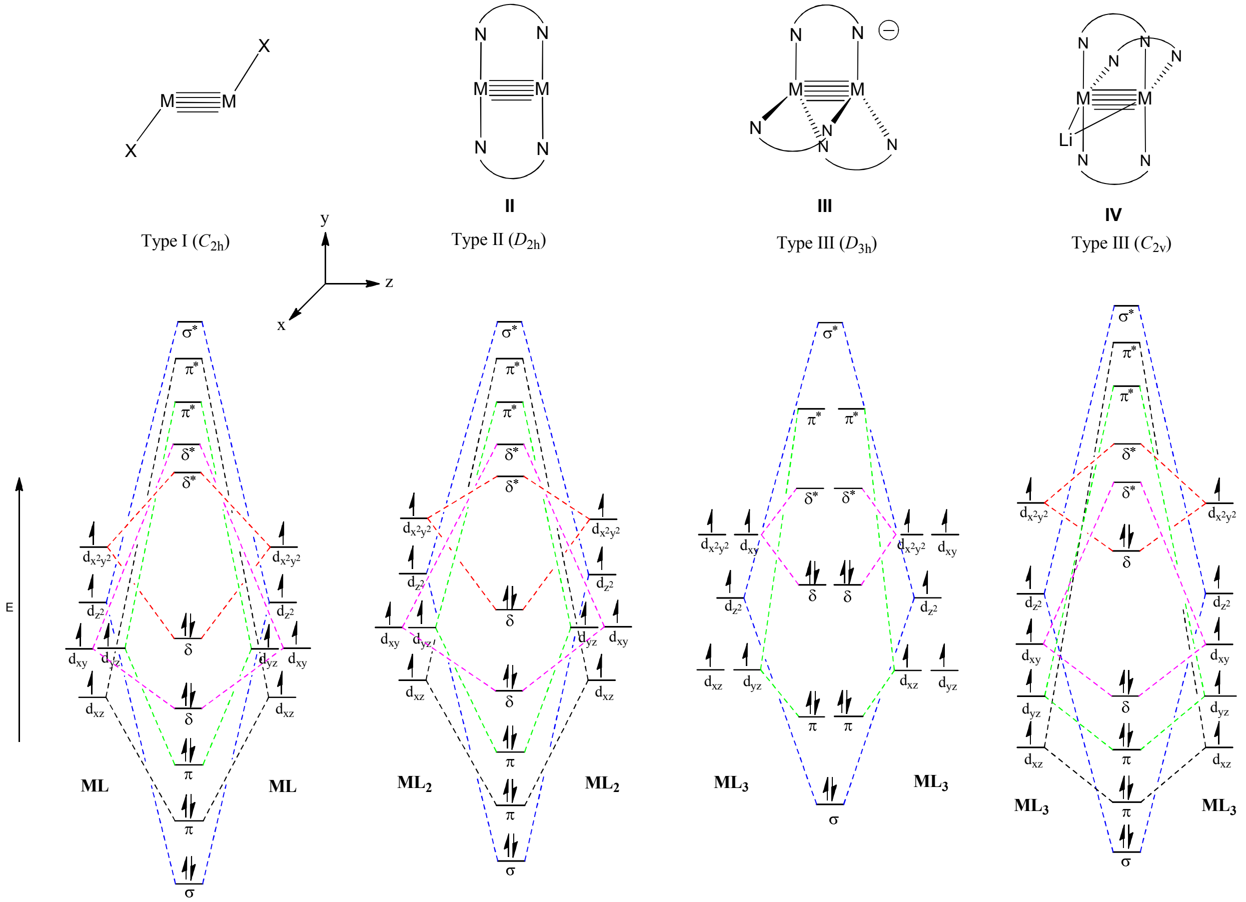
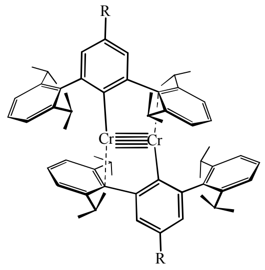


Figure 2. Possible geometries of the quintuple bonded dinuclear complexes and their corresponding qualitative MO diagrams.

Cite this: DOI: 10.1039/c0xx00000x

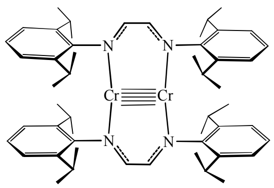
www.rsc.org/xxxxxx

ARTICLE TYPE



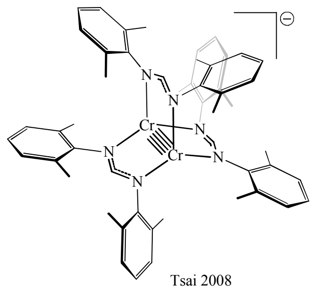
Power

1: R = H; **Cr-Cr = 1.8351(4) Å** in 2005
2: R = SiMe$_3$; **Cr-Cr = 1.8077(7) Å** in 2007
3: R = OMe; **Cr-Cr = 1.8160(5) Å** in 2007
4: R = F; **Cr-Cr = 1.831(2) Å** in 2007



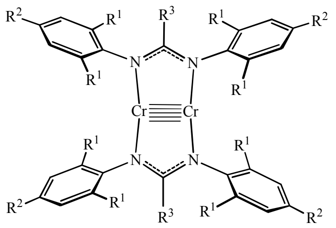
Theopold 2007

5: **Cr-Cr = 1.8028(9) Å**



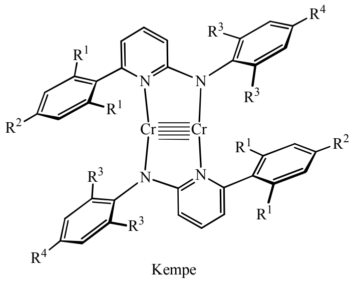
Tsai 2008

6: **Cr-Cr = 1.7397(9) Å**



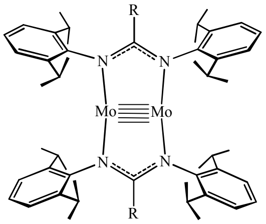
Tsai 2008

7: R^1= CH$_3$, R^2 = CH$_3$, R^3 = H; **Cr-Cr = 1.7404(8) Å**
8: R^1= Et, R^2 = R^3 = H; **Cr-Cr = 1.7454(1) Å**
9: R' = *i*-Pr, R^2 = R^3 = H; **Cr-Cr = 1.7472(10) Å**
10: R^1 = *i*-Pr, R^2 = H, R^3 = CH$_3$; **Cr-Cr = 1.7395(7) Å**



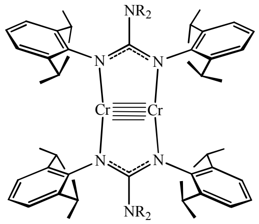
Kempe

11: R^1 = R^2 = *i*-Pr, R^3 = R^4 = Me; **Cr-Cr = 1.749(2) Å** in 2008
12: R^1 = Me, R^3 = *i*-Pr, R^2 = R^4 = H; **Cr-Cr = 1.750(1) Å** in 2009



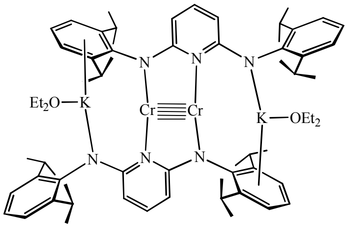
Tsai 2009

13: R = H; **Mo-Mo = 2.0187(9) Å**
14: R = Ph; **Mo-Mo = 2.0157(4) Å**



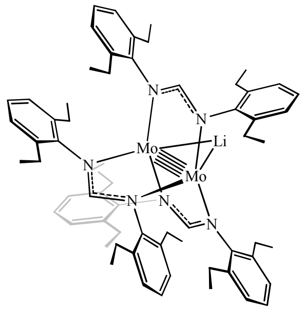
Kempe

15: NR$_2$ = N(CH$_3$)$_2$, **Cr-Cr = 1.7293(12) Å** in 2009
16: NR$_2$ = 2,6-(CH$_3$)$_2$C$_5$H$_8$N, **Cr-Cr = 1.7056(12) Å** in 2003



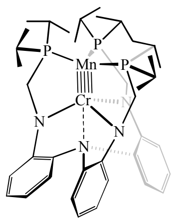
Tsai 2012

17: **Cr-Cr = 1.7443(10) Å**



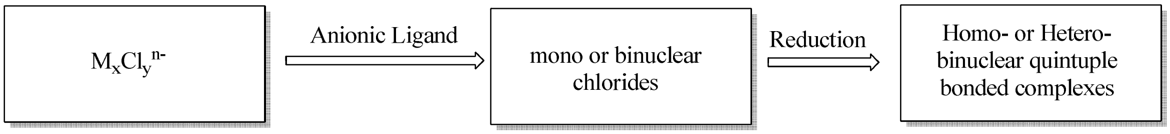
Tsai 2012

18: **Mo-Mo = 2.0612(4) Å**

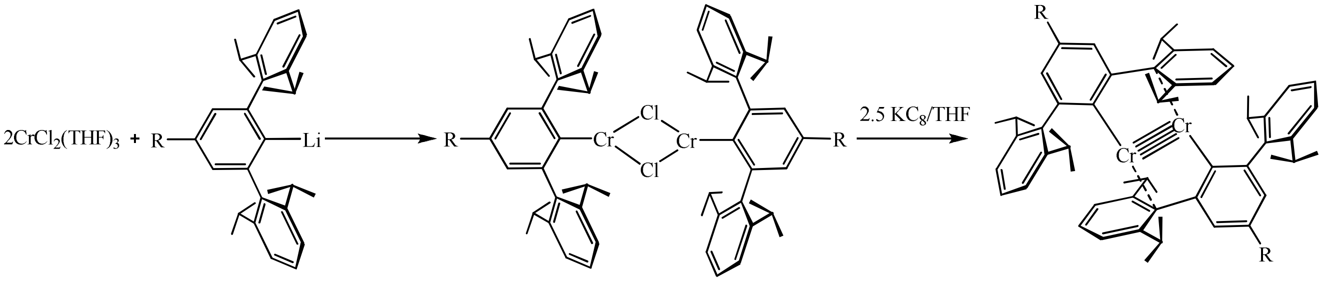


Lu 2013

Figure 3. Structurally characterized quintuple bonded complexes.



Scheme 1. A typical synthetic route of quintuple bonded complexes.

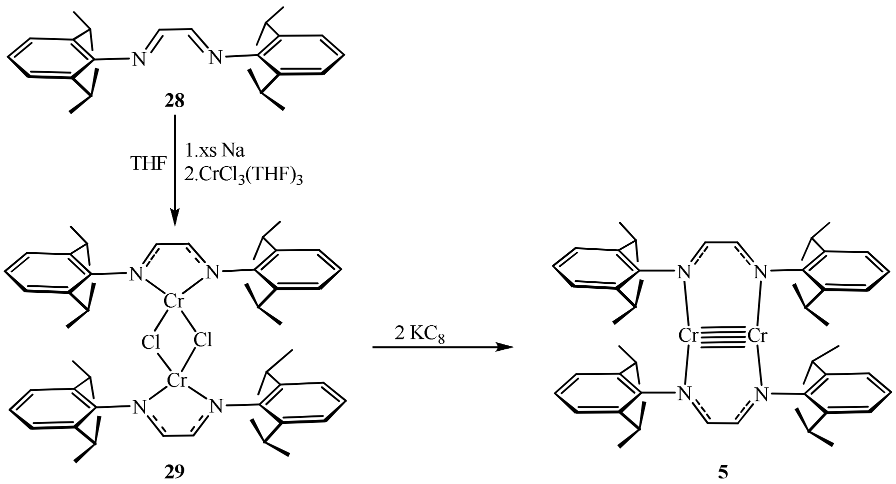


20: R = H, **21**: R = $SiMe_3$
22: R = OMe, **23**: R = F

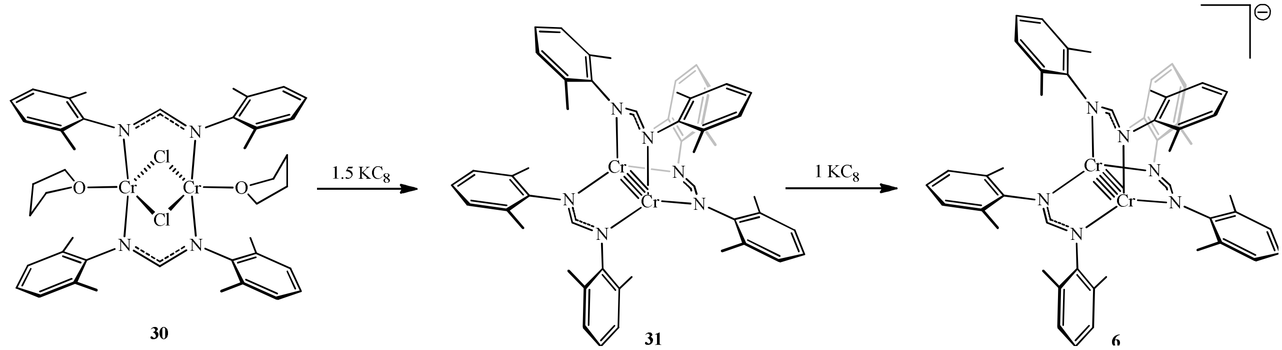
24: R = H, **25**: R = $SiMe_3$
26: R = OMe, **27**: R = F

1: R = H, **2**: R = $SiMe_3$
3: R = OMe, **4**: R = F

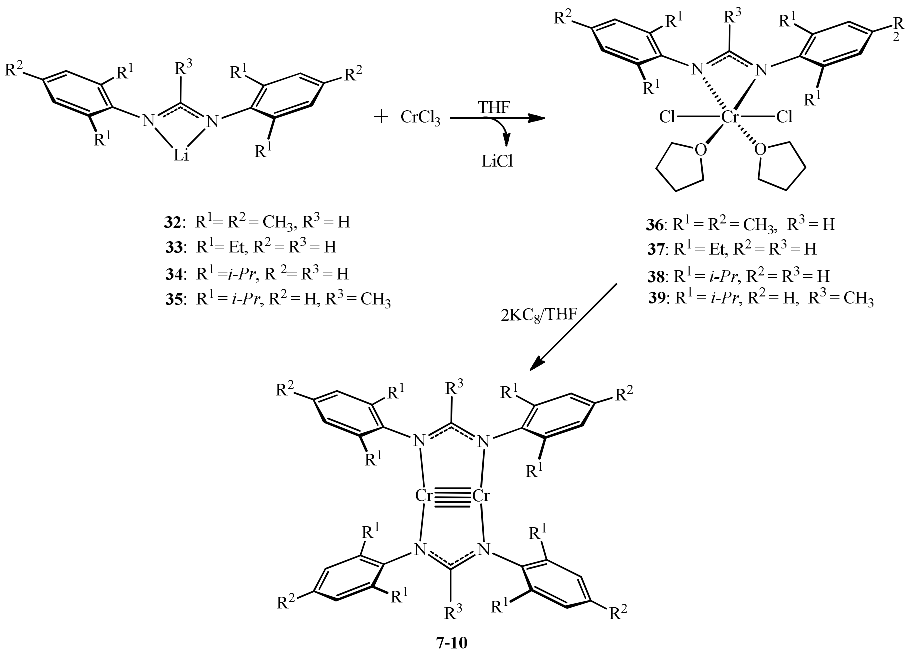
Scheme 2. Synthesis of the quintuple bonded complexes **1**-**4**.



Scheme 3. Synthesis of the quintuple bonded complex **5**.



Scheme 4. Synthesis of the lantern type quintuple bonded complex **6**.



32: $R^1 = R^2 = CH_3$, $R^3 = H$
33: $R^1 = Et$, $R^2 = R^3 = H$
34: $R^1 = i\text{-}Pr$, $R^2 = R^3 = H$
35: $R^1 = i\text{-}Pr$, $R^2 = H$, $R^3 = CH_3$

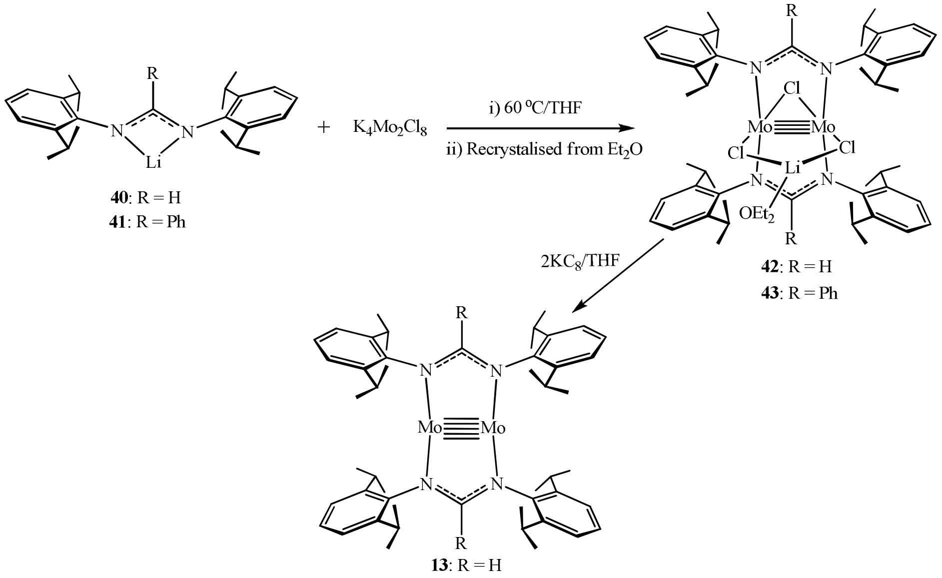
36: $R^1 = R^2 = CH_3$, $R^3 = H$
37: $R^1 = Et$, $R^2 = R^3 = H$
38: $R^1 = i\text{-}Pr$, $R^2 = R^3 = H$
39: $R^1 = i\text{-}Pr$, $R^2 = H$, $R^3 = CH_3$

Scheme 5. Synthesis of the quintuple bonded dimers **7-10**.

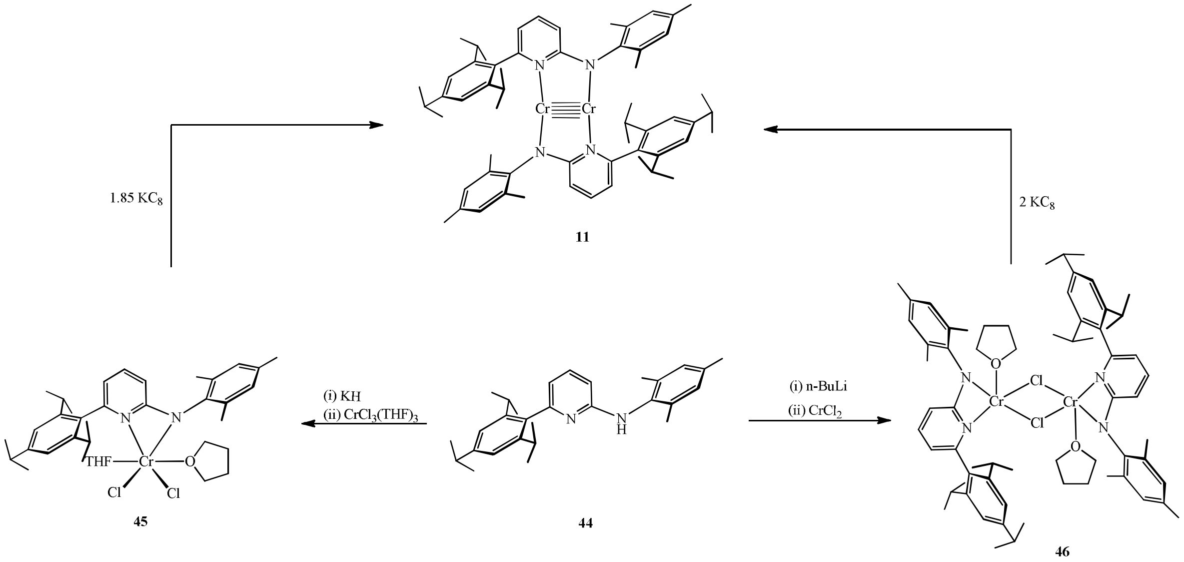
Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

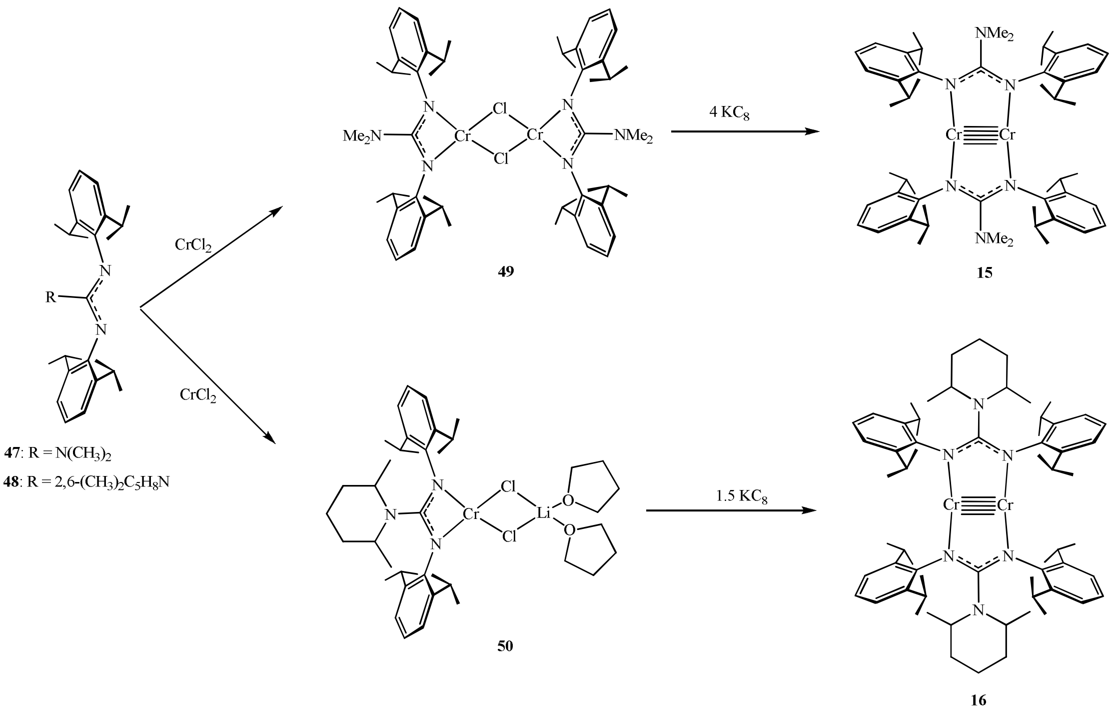
ARTICLE TYPE



Scheme 6. Synthesis of the first quintuple bonded dimolybdenum amidinate dimers **13** and **14**.

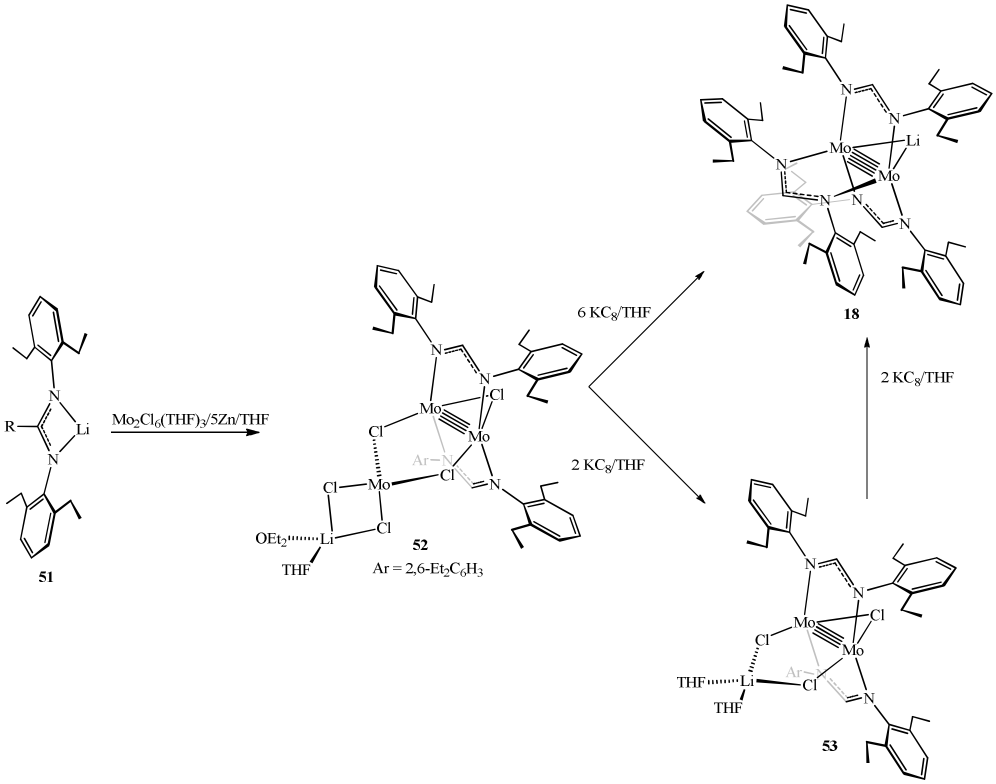


Scheme 7. Synthesis of the amidopyridine-supported quintuple bonded chromium complex **11**.

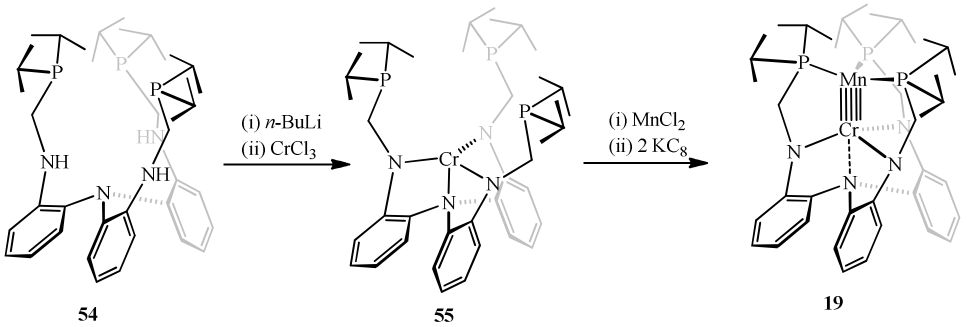


Scheme 8. Synthesis of the guanidinate-supported quintuple bonded dichromium complexes **15** and **16**.

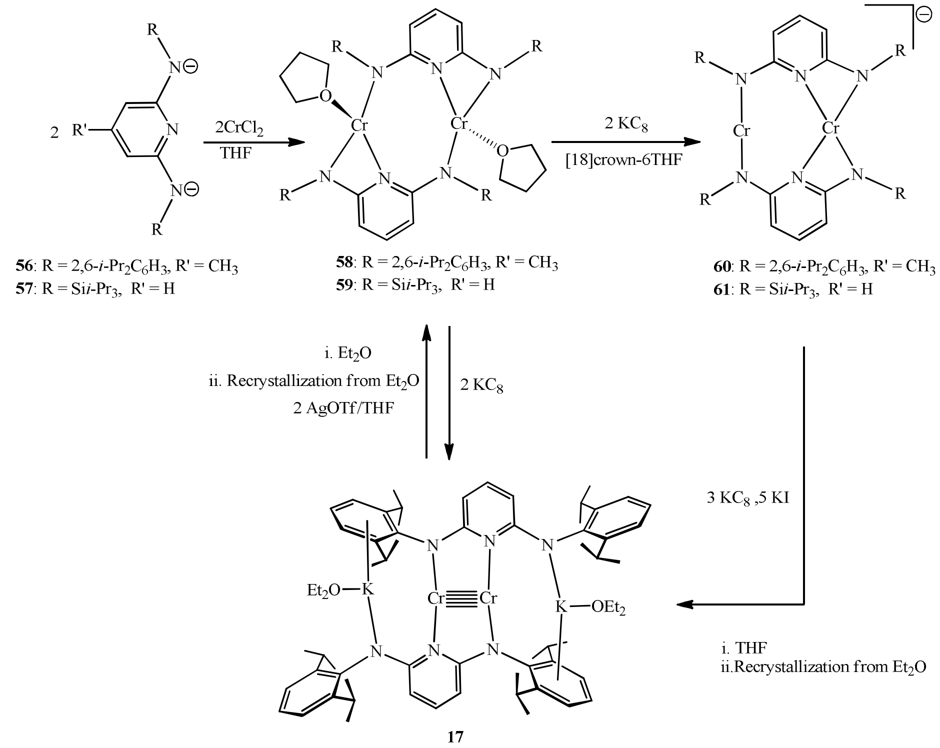
5



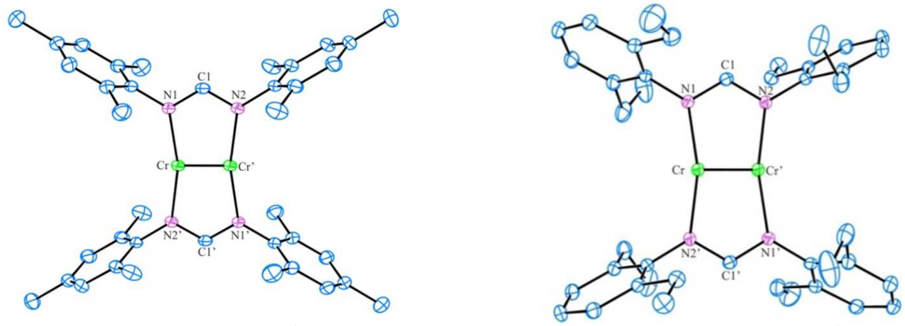
Scheme 9. Synthetic pathway for the Li-spanned quintuple bonded molybdenum complex **18**.



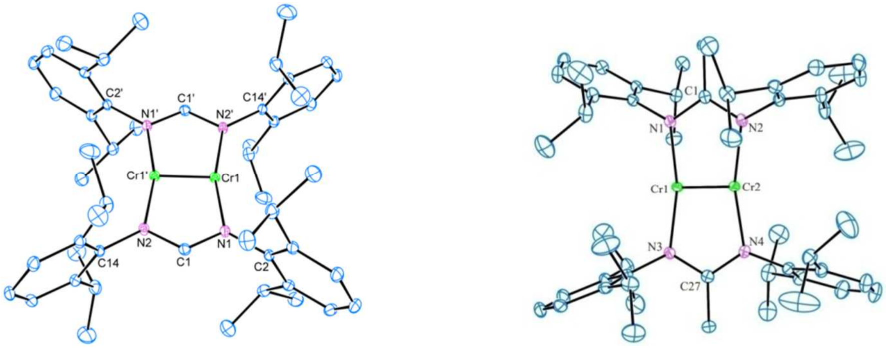
Scheme 10. Synthesis of the heterodinuclear quintuple bonded Cr-Mn complex **19**.



Scheme 11. Synthesis of the quintuple bonded dichromium complex **17**.

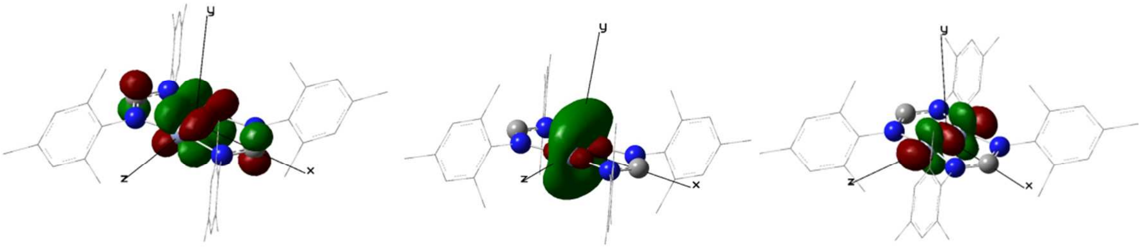


7 (Cr-Cr = 1.7404(8) Å) **8** (Cr-Cr = 1.7454(1) Å



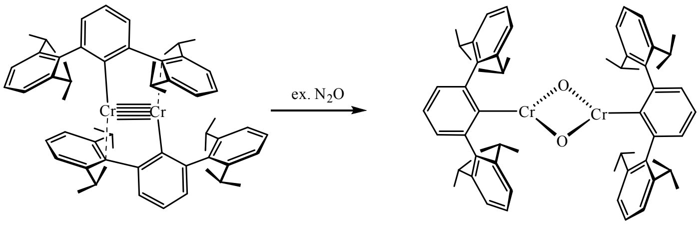
9 (Cr-Cr=1.7472(10)Å) **10** (Cr-Cr = 1.7395(7) Å)

Figure 4. The solid-state molecular structures of the complexes **7**-**10**.



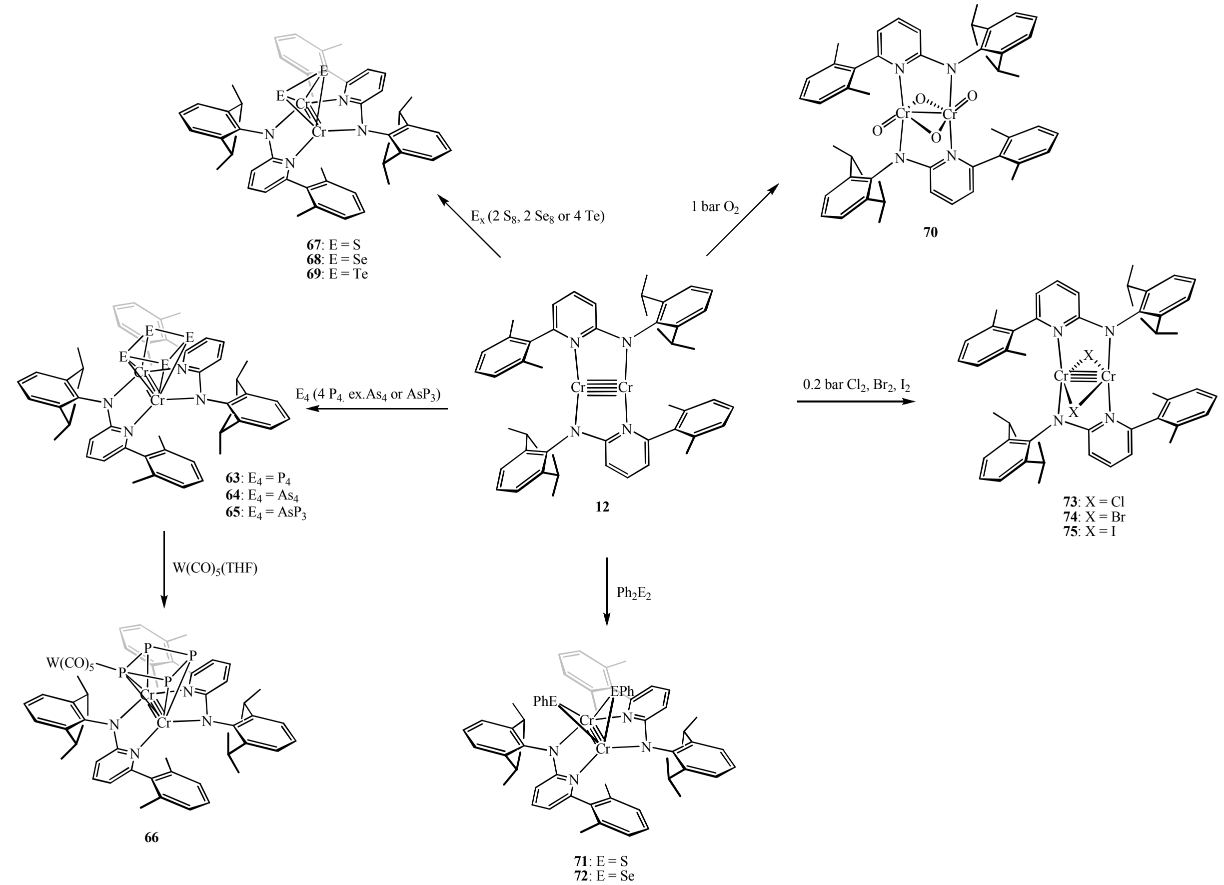
HOMO (-3.814 eV) HOMO-1 (-3.980 eV) HOMO-2 (-5.073 eV)

Figure 5. Frontier orbitals displaying Cr-Cr bonding in the complex **7**.

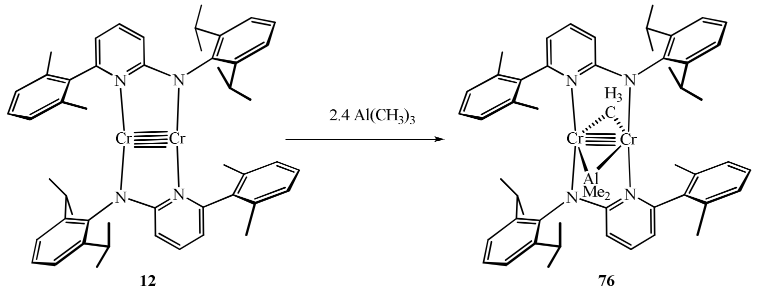


1 **62**

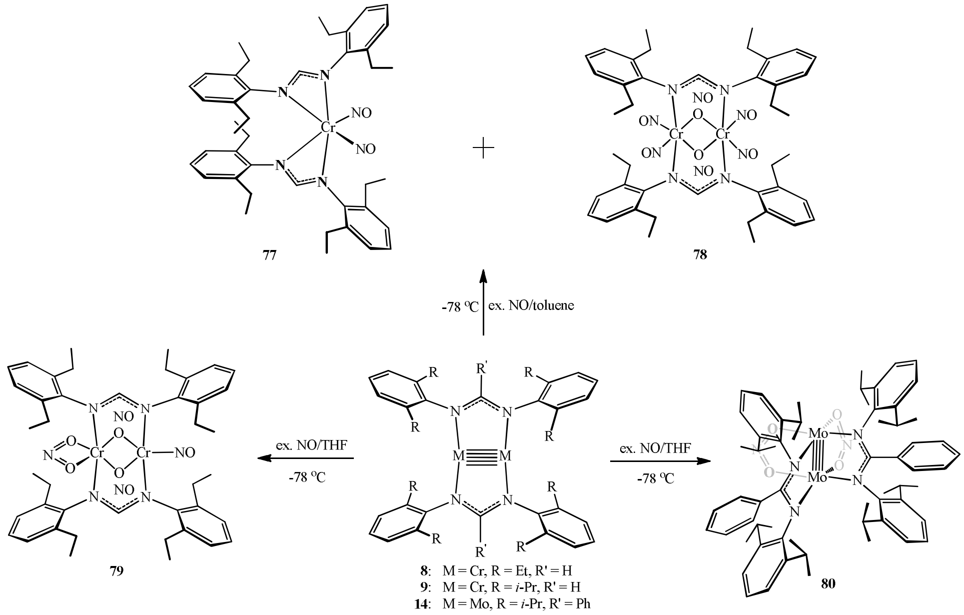
Scheme 12. Oxygenation of **1** with N_2O.



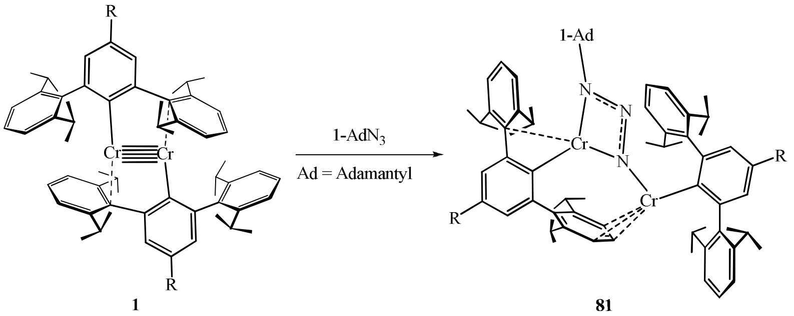
Scheme 13. Reactions of **12** with pnictogens, chalcogens and halogens.



Scheme 14. Carboallumination reaction of the complex **12**.



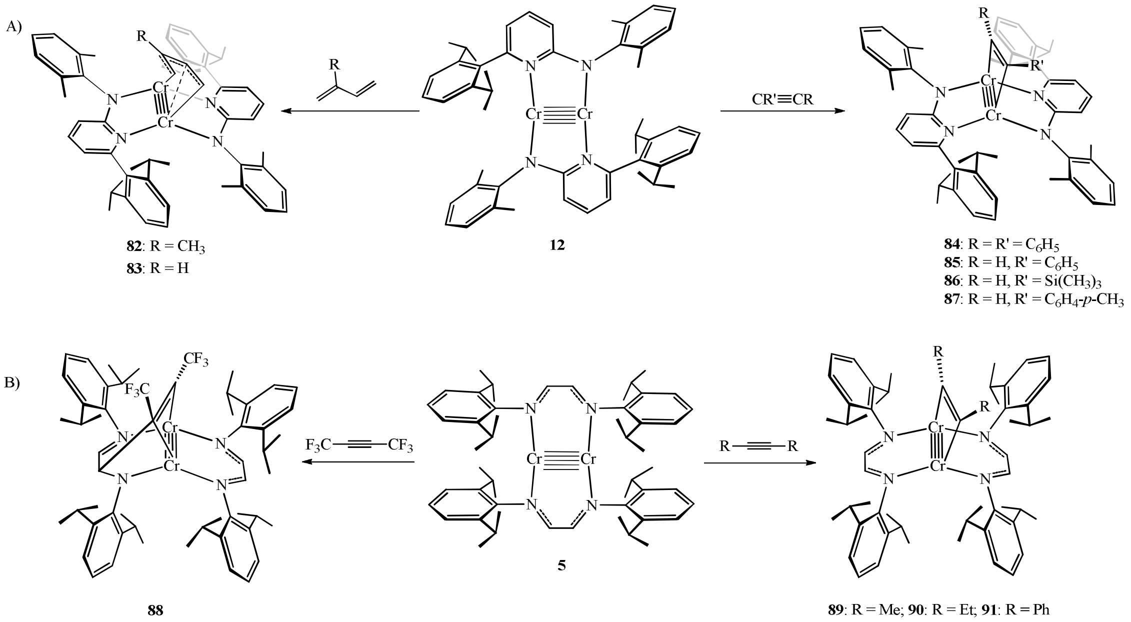
Scheme 15. Reactions of the complexes **8**, **9** and **14** with NO.



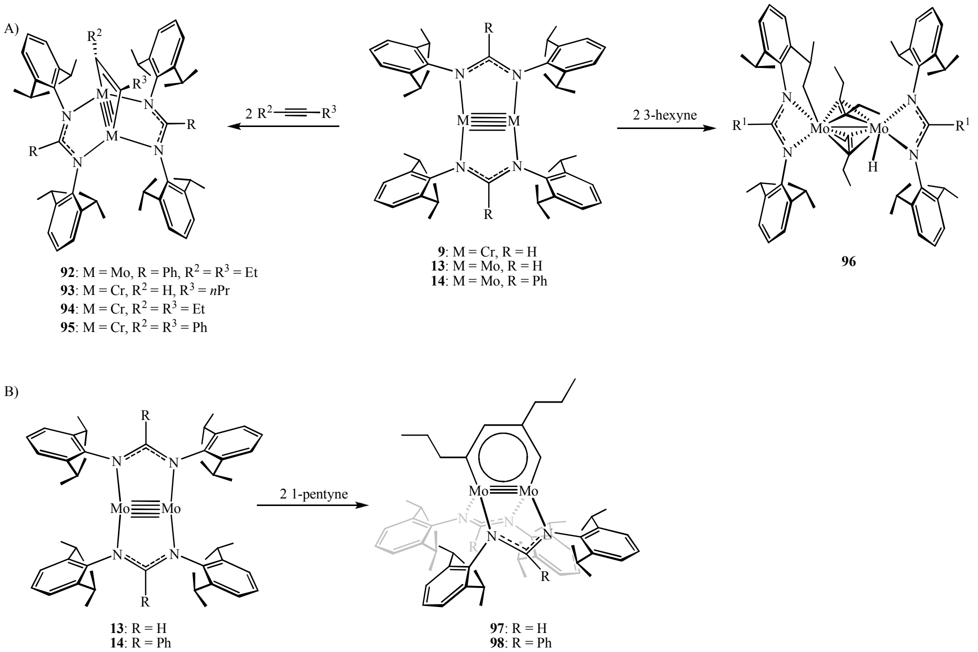
Scheme 16. Reaction of **1** with 1-AdN$_3$.

Cite this: DOI: 10.1039/c0xx00000x

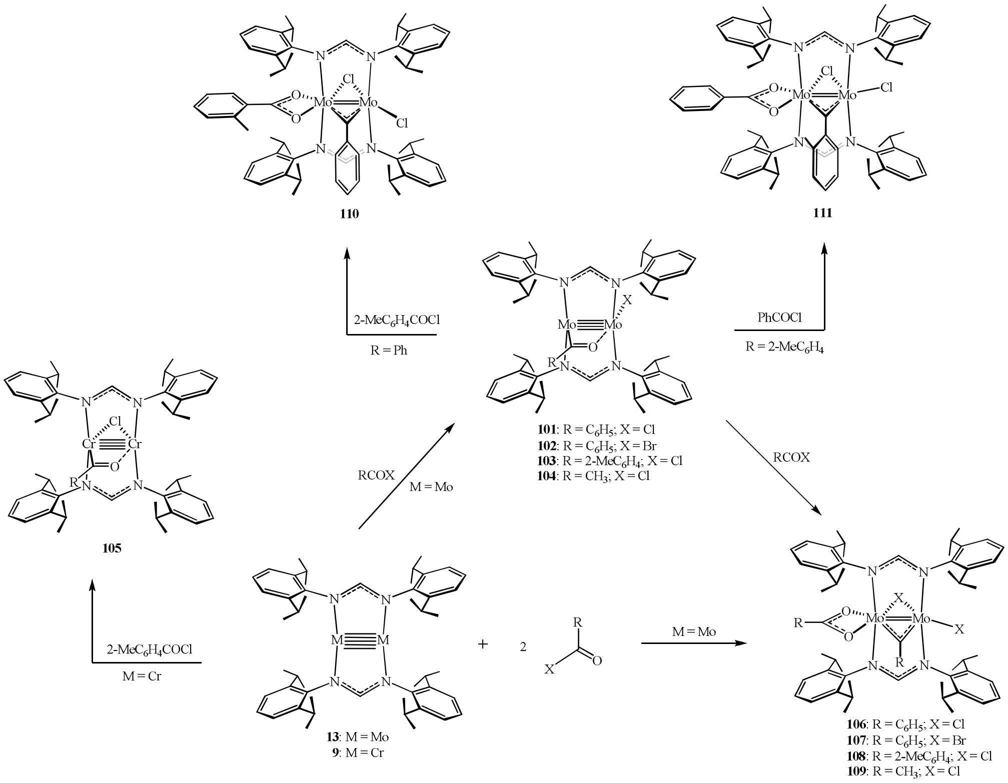
www.rsc.org/xxxxxx



Scheme 17. A) Reactions of **12** with dienes and alkynes, and B) reactions of **5** with alkynes.



Scheme 18. A) Reactions of **9**, **13** and **14** with alkynes, and B) [2+2+2] cycloaddition of **13** and **14** with 1-pentyne.



Scheme 19. Reactions of **9** and **13** with acyl halides.