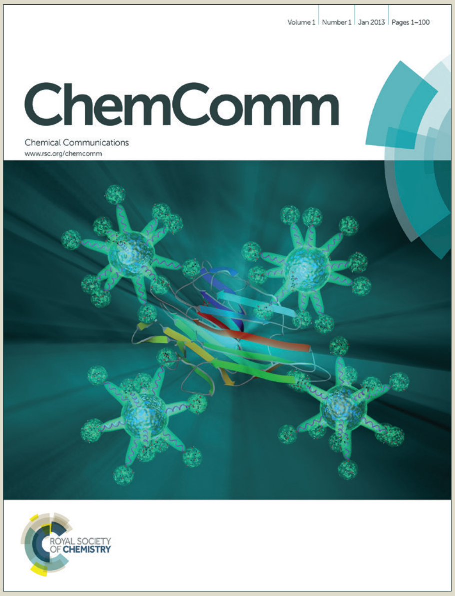
ChemComm

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/chemcomm

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Discovering Complexes Containing a Metal-Metal Quintuple Bond: From Theory to Practice

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

Received (in XXX, XXX) XthXXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

Whereas the field of the metal-to-metal multiple bonding was considered mature, it was recently reinvigorated by the discovery of quintuple bonded dinuclear complexes. Initiated by theoretical studies, the quintuple bonding was promoted by the recognition of the first isolable quintuple bonded chromium phenyl dimer Ar'CrCrAr' (Ar' = 2,6-(2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$C$_6$H$_3$) by Power and co-workers in 2005. Soon afterwards, many dinuclear group VI metal-to-metal quintuple bonded complexes stabilized by sterically hindered N-based bidentate ligands were subsequently characterized. All these remarkable compounds feature two or three bridging ligands, so each metal is two to three coordinate with respect to the ligands. Of particular interest is that they all have extremely short metal-metal bond lengths. These low-coordinate homo-univalent quintuple bonded dinuclear species not only display remarkable bonding schemes between two metal atoms, but also show interesting reaction chemistry with unsaturated hydrocarbons and small inorganic molecules. Herein, we review recent advances in the quintuple bond chemistry including synthesis, characterization and reactivity of the quintuple bonded complexes.

Introduction

According to Lewis's theory of a covalent bond, the bonding electrons are considered to be localized between two atoms.[1] This bond is not only limited to one but also multiple, and the term "bond order" was introduced to measure the number of bonds between a pair of atoms. The maximum bond order of a covalent bond between two main group elements is known to be three for two nitrogen atoms in molecular nitrogen and two carbon atoms in alkyne molecules, for example. Discovery of molecules with chemical bonds of higher bond orders always fascinates chemists. To this end, chemists drove their attentions to transition metals, which have 9 valence orbitals, namely, 1s, 3p and 5d. In fact, initially, the transition metal chemistry was not considered even though they occupy half of the periodic table. After Werner's great contributions in coordination chemistry,[2-5] the transition metal chemistry was recognized rapidly. As a result, before mid-1960s, the transition metal chemistry was mainly governed by his theory.[6-10] During that time, polynuclear complexes were recognized and a huge number of complexes were extensively studied by Werner.[11] However, the direct metal-metal interaction was not known until the characterization of the trinuclear complex [Re$_3$Cl$_{12}$]$^{3-}$ in 1963,[3-5] which contains three Re–Re double bonds.

The recognition of the first quadruple bonded dirhenium complex [Re$_2$Cl$_8$]$^{2-}$ by Cotton and co-workers in 1964[12] initiated a huge rush for multiple bonding. Since then, a large number of quadruply bonded complexes have been characterized in the past 50 years.[2] However, the quest for molecules having higher bond order chemical bonds has never stopped. Matrix isolation was proven to be a good way to probe the diatomic transition element species M$_2$ (M = Cr, Mo) by host guest matrices at low temperatures. A sextuple bond (2σ, 2π and 2δ) has been proposed to these simple diatomic molecules. Unfortunately, they cannot be isolated and structurally characterized.[13-17] To accomplish the goal of identifying complexes with metal-metal bond orders higher than four, scientists turned their attentions to the quintuple bonded species. On the theoretical side, in 1979, Hoffmann and co-workers suggested that those M$_2$L$_6$ molecules with D_{3h} symmetry possibly have a metal-metal quintuple bond.[18] Furthermore, Weinhold and Landis introduced natural bond orbital (NBO) theory and localized concepts to species, which are difficult to understand their bonding.[19] They extended these concepts to transition metals via drawing Lewis-like structures and bonding concepts.[19, 20] Based on their theory, they suggested the most probable geometry of a quintuple bonded dinuclear complex be *trans*-bent with C_{2h} symmetry.

On the experimental side, the landmark achievement of the invention of the isolable molecule Ar'CrCrAr' (Ar' = 2,6-(2,6-^{i}Pr$_2$C$_6$H$_3$)C$_6$H$_3$) (**1**) by Power[21] and co-workers in 2005 gave boost for chemists to more focus on to exploring the quintuple bonding chemistry. Afterwards, several quintuply bonded species have been characterized.[22-31] Based on theoretical calculations and structural characterizations, three possible geometries, namely, type I, II and III were accordingly concluded (Figure 1) for the quintuple bonded complexes. The type II complexes predominate in the field of quintuple bond chemistry, while there are only two examples of type III compounds[23, 29, 31] featuring paddlewheel architecture.

((Fig. 1))

In order to maximize the bond order between two metal centres, few points should be considered. As shown in Figure 1, it is imperative that the metals have a d^5 electronic configuration. Secondly, all five d orbitals are evenly occupied; that is, each metal fragment has a high spin configuration, which is strongly associated with the number and field strength of the ligands. Since the ligands are a crucial factor to the stability of the multiply bonded metal units. To reduce the participation of the metal d orbitals in σ bonding to the ligands, the number of ligands must be minimized. Strong σ-donor ligands significantly raise energy of the σ* orbitals (mainly the metal d orbitals), which consequently results in a low-spin metal centre, so they should not be used for the stabilization of the quintuple bonded bimetal units. In addition, the employment of π-donor and -acceptor ligands should be avoided as well, since metal-ligand π bonding decreases overlap between two metal centres[32]. In other words, to maximize the metal-metal quintuple bonding interactions and obviate oligomerization of the quintuple bonded bimetal units, the use of voluminous ligands is necessary. Accordingly, six types of ligand scaffolds have been employed for this regard (Figure 2).

((Fig. 2))

This feature article surveys the recent developments in the quintuple bond chemistry. After Power's contributions in 2005, a number of nitrogen donor-stabilized quintuply bonded complexes were reported. In 2007, Theopold isolated the chromium diazadiene dimer $[\kappa^2\text{-}(HCN\text{-}2,6\text{-}{}^iPr_2C_6H_3)_2Cr]_2$ (**6**).[22] After that, in 2008, Tsai and co-workers isolated a remarkable type III dichromium quintuple bonded complex $[Cr_2\{CH(N\text{-}2,6\text{-}Me_2\text{-}C_6H_3)_2\}_3]^-$ (**11**).[23] During the same year, Tsai and co-workers described four more amidinate-supported quintuply bonded dichromium species $[Cr\{\mu\text{-}RC(N\text{-}Ar)_2\}]_2$, (R = H, Ar = $2,4,6\text{-}Me_3C_6H_2$ (**16**), R = H, Ar = $2,6\text{-}Et_2C_6H_3$ (**17**), R = H, Ar = $2,6\text{-}{}^iPr_2C_6H_3$ (**18**), R = Me, Ar = $2,6\text{-}{}^iPr_2C_6H_3$ (**19**)).[24] Meanwhile, Kempe's pyridylamido-stabilized dichromium species $[Cr\text{-}\mu\text{-}Ar]_2$ (Ar = $2\text{-}(N\text{-}2,4,6\text{-}Me_3C_6H_2)\text{-}6\text{-}(2,4,6\text{-}{}^iPr_3C_6H_2)\text{-}C_5H_3N$ (**23**), $2\text{-}(N\text{-}2,6\text{-}Me_2C_6H_3)\text{-}6\text{-}(2,6\text{-}{}^iPr_2C_6H_3)\text{-}C_5H_3N$ (**24**))[25, 26] were also documented. All these structurally characterized complexes (**6**, **11**, **16-19**, **23** and **24**) show ultrashort Cr–Cr bond lengths in the range of 1.83-1.73 Å. In 2009, Kempe and co-workers showed a guanidinate-stabilized quintuply bonded dichromium complex $[Cr\{\mu\text{-}RC(N\text{-}Ar)_2\}]_2$, (R = NMe_2, Ar = $2,6\text{-}{}^iPr_2C_6H_2$ (**28**), featuring the shortest Cr–Cr bond length of 1.7293(12) Å.[28] Most recently the same group of members also reported a guanidinate based quintuply bonded dichromium complex $[Cr\{\mu\text{-}RC(N\text{-}Ar)_2\}]_2$, (R = $2,6\text{-}Me_2NC_5H_8$, Ar = $2,6\text{-}{}^iPr_2C_6H_2$ (**30**)) which is the shortest Cr–Cr bond length of 1.7056 (12) Å to date.[33] Down the periodic table, Tsai's group extended the quintuple bonded complexes from chromium to molybdenum. In 2009, they identified the first quintuply bonded dimolybdenum complexes **48** and **49**.[27] During the preparation of this manuscript, Lu and co-workers reported a trisphosphinotrisamidoamine-supported heterodinuclear quintuply bonded Cr–Mn species $[MnCr(NN_3P_3)]$ (**43**) ($NN_3P_3 = N(o\text{-}(N\text{-}CH_2P^iPr_2)C_6H_4)_3$).[31]

Syntheses of the quintuple bonded dichromium and dimolybdenum complexes

Synthesis of the quintuple bonded complexes was initiated by Power's group by the isolation of **1** in 2005.[21] Later on, the group VI metal-to-metal quintuple bonds stabilized by N-based ligands were subsequently described.[22-30] The synthetic strategies are in principle similar but the supporting ligand differentiates. In general, the first step is the reaction of the lithiated ligands with appropriate metal chloride (MCl_n, M= Cr, Mo) to produce the chloro-bridged dimers $[LM(\mu\text{-}Cl)]_2$(L is the supporting ligand) or the mononuclear dichloro species $LMCl_2(THF)_2$, which are further reduced by strong reducing agents to engender the formation the quintuple bonded complexes (Scheme 1). The key synthetic step is analogous to Wurtz reductive coupling reaction in a way that the corresponding ligand-supported metal chlorides are reduced to the quintuple bonded dinuclear complexes. It is noteworthy that all precursors with ligands of chelating coordination mode were transformed into the quintuple bonded dinuclear complexes with bridging style ligands after reduction. Moreover, none of these precursors show Cr–Cr bonding interactions.

((Scheme 1))

Power's quintuple bonded chromium phenyl dimer **1** was obtained in 41% yield by KC_8 reduction of the chloro-bridged dichromium precursor (Scheme 2).[21] To understand how the electronic and steric factors affect the Cr–Cr quintuple bond length, they prepared three chromium phenyldimers $[Cr(2,6\text{-}\{2,6\text{-}{}^iPr_2C_6H_3\}_2\text{-}4\text{-}R\text{-}C_6H_2]_2$ (R = Me_3Si (**2**), OMe (**3**), F (**4**)), where three electronically and sterically different groups were incorporated into the *para* positions of the central phenyl rings of the ligands.[34] The X-ray crystallographic data showed that all Cr–Cr bond lengths in **2-4** are in the range of 1.8077(7) and 1.8351(4) Å, and Power suggested this variation be due to packing instead of electronic effect.

((Scheme 2))

After Power described the characterization of complexes **2-4** in 2007,[34] Theopold and co-workers applied the same strategy to prepare the quintuply bonded dichromium complex **6** based on the redox non-innocent diazadiene ligand (Scheme 3).[22] Complex **6** was obtained from the reduction of its corresponding dark green dinuclear precursor $[\kappa^2\text{-}(HCN\text{-}2,6\text{-}{}^iPr_2C_6H_3)_2Cr(\mu\text{-}Cl)]_2$ (**5**) with KC_8.

((Scheme 3))

Due to the ease to tune their steric and electronic properties, amidinates have emerged as popular ligands for the synthesis of multiple bonded dinuclear complexes.[2] Tsai's group has been successful in making use of amidinates as supporting ligands to prepare the quintuple bonded dinuclear species. The employment of amidinates to support the quintuple bonded dichromium units in Tsai's group was actually from the characterization of the first low-coordinate quadruple bonded dimolybdenum complex $Mo_2[\mu\text{-}\kappa^2\text{-}Me_2Si(N\text{-}2,6\text{-}{}^iPr_2\text{-}C_6H_3)_2]_2$ (**8**),[32] which was obtained upon Na/Hg reduction of *cis*-1,2-$Mo_2Cl_2[\mu\text{-}\kappa^2\text{-}Me_2Si(N\text{-}(2,6\text{-}{}^iPr_2\text{-}C_6H_3)_2]_2$ (7) (Scheme 4). In **8**, the dimolybdenum unit is stabilized by two π-donating bidentate diamido ligands and the Mo–Mo bond length 2.1784(12) Å is slightly longer than the regular Mo–Mo quadruple bond length.[2] In contrast to the numerous quadruple bonded dinuclear species featuring a tetragonal configuration,[2] complex **8** represents the first and only example, whereby each metal is two coordinate with respect to the ligands. DFT calculations on **8** revealed strong ligand-to-metal N–Mo π interactions (HOMO–11). To reduce the ligand-to-metal π bonding observed in **8**, Tsai and his co-workers turned their attentions to the less π donating amidinates for the construction of the quintuple bonded dinuclear complexes.

((Scheme 4))

In 2008, Tsai and co-workers reported the characterization of the novel quintuple bonded dichromium complex **11**, where the Cr_2^{2+} unit was surrounded by three amidinates leading to paddlewheel architecture. As shown in Scheme 5, KC_8 reduction of the homodivalent dichromium amidinate $[\{Cr(THF)\}_2(\mu\text{-}Cl)_2\{\mu\text{-}\kappa^2\text{-}HC(N\text{-}2,6\text{-}Me_2C_6H_3)_2\}_2]$ (**9**) resulted in the formation of the neutral paramagnetic mixed-valent dichromium (Cr^I, Cr^{II}) precursor $[Cr_2\{HC(N\text{-}2,6\text{-}Me_2C_6H_3)_2\}_3]$ (**10**). Magnetic measurements indicated that **10** have one unpaired electron, which implied the formal bond order of the Cr–Cr bond is 4.5. Accordingly, the addition of one electron to **10** could lead to the formation of a diamagnetic quintuple bonded lantern species. Indeed, subsequent KC_8 reduction of **10** with the presence of crypt-[222] resulted in the isolation of the diamagnetic **11** in 83% yield,[23] which suggested that all d electrons pair up to form the Cr–Cr quintuple bond.

((Scheme 5))

Continuing their journey in exploring the quintuple bonding, Tsai and co-workers in 2008 prepared four quintuple bonded chromium amidinate dimers **16-19** (Scheme 6).[24] Compounds **16-19** were synthesized starting from a series of paramagnetic mononuclear chromium compounds $CrCl_2(THF)_2\{\kappa^2\text{-}RC[NAr]_2\}$ (R = H, Ar = $2,4,6\text{-}Me_3C_6H_2$ (**12**), R = H, Ar = $2,6\text{-}Et_2C_6H_3$ (**13**), R = H, Ar = $2,6\text{-}{}^iPr_2C_6H_3$ (**14**), R = Me, Ar = $2,6\text{-}{}^iPr_2C_6H_3$ (**15**)). Subsequent reduction of **12-15** with KC_8 in THF gave rise to the formation of **16-19**, respectively.

((Scheme 6))

During the same year of 2008, Kempe and co-workers described the characterization of two pyridylamido-stabilized quintuple bonded dichromium complexes **23** and **24**[25, 26] (Scheme 7). To prepare these two species, they synthesized the mononuclear species $CrCl_2(THF)_2[2\text{-}(N\text{-}2,4,6\text{-}Me_3C_6H_2)\text{-}6\text{-}(2,4,6\text{-}{}^iPr_3C_6H_2)\text{-}C_5H_3N]$ (**20**), and the two chloro-bridged dinuclear compounds $[Cr(\mu\text{-}Cl)(THF)_2\{2\text{-}(N\text{-}2,4,6\text{-}{}^iPr_3C_6H_2)\text{-}6\text{-}(2,4,6\text{-}Me_3C_6H_2)\text{-}C_5H_3N\}]_2$ (**21**) and $[Cr(\mu\text{-}Cl)(THF)_2\{2\text{-}(N\text{-}2,6\text{-}{}^iPr_2C_6H_3)\text{-}6\text{-}(2,6\text{-}Me_2C_6H_3)\text{-}C_5H_3N\}]_2$ (**22**) from the reaction of pyridylamido ligands $[2\text{-}(N\text{-}2,6\text{-}{}^iPr_2C_6H_2R^2)\text{-}6\text{-}(2,6\text{-}Me_2C_6H_2R^1)\text{-}C_5H_3N$ ($R^1 = R^2$ = H, Me, ^iPr)] with two different metal precursors, namely $CrCl_2$ and $CrCl_3$. **23** and **24** were obtained by the reduction of **20-22** with KC_8 (Scheme 7). The same group also employed sterically encumbering guanidinate ligands for the synthesis of the quintuple bonded dichromium species **28** and **30**. As illustrated in Scheme **8**, the reaction of lithiated guanidinate ligands $[RC(N\text{-}Ar)_2Li]$ (R = NMe_2, Ar = $2,6\text{-}{}^iPr_2C_6H_2$ (**25**), R = $2,6\text{-}Me_2NC_5H_8$, Ar = $2,6\text{-}{}^iPr_2C_6H_2$ (**26**)) with CrCl2 in THF resulted in the formation Cr(II) and Cr(II)-ate complexes $[Cr(\mu\text{-}Cl)RC(N\text{-}Ar)_2]_2$ (R = NMe_2, Ar = $2,6\text{-}{}^iPr_2C_6H_2$ (**27**)), $[Cr(\mu\text{-}Cl)_2RC(N\text{-}Ar)Li(THF)_2]$ (R = $2,6\text{-}Me_2NC_5H_8$, Ar = $2,6\text{-}{}^iPr_2C_6H_2$) (**29**)), respectively. Subsequent reduction of **27** and **29** with KC_8, the ultra-short guanidinate supported quintuply bonded dichromium complexes **28** and **30**, respectively, were yielded (Scheme 8).[28, 33]

((Scheme 8))

Building up a quintuple bond between two metal atoms from their halide precursors, either a mononuclear $[LCrCl_2(THF)_2]$ or a dinuclear $[LCr(\mu\text{-}Cl)]_2$ (L = monodentate or bidentate) is now well known. Recently, Tsai and co-workers developed a synthetic route to the construction of the quintuple bonded dichromium complex in a stepwise manner. Noteworthy is that all precursors were halide-free, except for the $CrCl_2$ starting material.[30] As shown in Scheme 9, the reaction of the dilithiated 2,6-diamidopyridine $Li_2[2,6\text{-}(2,6\text{-}{}^iPr_2C_6H_3\text{-}N)_2\text{-}4\text{-}CH_3C_5H_2\text{-}N]$ (**31**) and $Li_2[2,6\text{-}({}^iPr_3SiN)_2\text{-}C_5H_3N]$ (**32**) with $CrCl_2$ resulted in the formation of the respective dinuclear complexes $[\{(THF)Cr(\mu\text{-}\kappa^1\text{:}\kappa^2\text{-}2,6\text{-}(2,6\text{-}{}^iPr_2C_6H_3\text{-}N)_2\text{-}4\text{-}CH_3C_5H_2N)\}_2]$ (**33**) and $[\{(THF)Cr(\mu\text{-}\kappa^1\text{:}\kappa^2\text{-}2,6\text{-}({}^iPr_3SiN)_2\text{-}C_5H_3N)\}_2]$ (**34**) in good yields. Both **33** and **34** displayed antiferromagnetic exchange between two Cr atoms and showed distinct structural conformations. Reduction of **33** and **34** with 2 equiv of KC_8 in the presence of 18-crown-6 ether yielded the mixed-valent dinuclear compounds $[(Et_2O)K@18\text{-}C\text{-}6][Cr\{\mu\text{-}\kappa^1\text{:}\kappa^2\text{-}2,6\text{-}(2,6\text{-}{}^iPr_2C_6H_3\text{-}N)_2\text{-}4\text{-}CH_3C_5H_2N\}_2Cr]$ (**35**) and $[(THF)_2K@18\text{-}C\text{-}6][Cr\{\mu\text{-}\kappa^1\text{:}\kappa^2\text{-}2,6\text{-}({}^iPr_3SiN)_2C_5H_3N)\}_2Cr]$ (**36**), respectively. Unlike **33** and **34**, compounds **35** and **36** displayed a similar structural configuration and exhibit antiferromagnetic coupling between two Cr atoms resulting in little useful NMR information. Interestingly, **33**, **35** and **36** show different reactivity towards KC_8 reduction. The quintuply bonded dichromium compound $[\{(Et_2O)K\}_2\{Cr_2(\mu\text{-}\kappa^1\text{:}\kappa^1\text{:}\kappa^1\text{:}\eta^3\text{:}\eta^6\text{-}2,6\text{-}(2,6\text{-}{}^iPr_2C_6H_3\text{-}N)_2\text{-}4\text{-}CH_3C_5H_2N)_2\}]$ (**37**) was directly isolated upon reduction of **33** with 2.5 equiv of KC_8, while in the case of **34**, no reaction occurs. Moreover, **37** could be prepared by addition of 3 equiv of KC_8 to **35** with the presence of 5 equiv of KI, whereas in the case of **36**, no Cr–Cr quintuple bond was formed with the same procedure. The presence of two potassium ions is crucial for the stabilization of the Cr–Cr quintuple bond in **37**. Notably, the Cr–Cr quintuple bond in **37** is prone to cleavage upon oxidation. Treatment of **37** with two equiv of AgOTf gave back to **33**. The characterization of **35** and **36** might shed some light on the formation mechanisms of the reported quintuple bonded dichromium species. Meanwhile, Tsai and co-workers discovered a new principle in the quintuple bonding chemistry: an axial coordination readily resulted in the destruction of the quintuple bond.

((Scheme 9))

Very recently, Lu and coworkers succeeded in synthesizing the hetero dinuclear quintuple bonded Cr–Mn complex **43**, stabilized by a heptadentate double-decker N-P hybridized trisphosphinotrisamidoamine ligand $N(o\text{-}({}^iPr_2PCH_2N)C_6H_4)_3$ (NN_3P_3) (Scheme 10). Lu's group demonstrated a unique synthetic protocol for the preparation of NN_3P_3-supported heterodinuclear multiple bonded complexes.[31, 35] As illustrated in Scheme 10, the first step was to construct the mononuclear Cr(III) complex $[Cr(\kappa^4\text{-}N(o\text{-}({}^iPr_2PCH_2N)C_6H_4)_3]$ (**42**) by mixing the lithiated $H_3[NN_3P_3]$ ligand (**41**) with $CrCl_3$ in THF. In **42**, the Cr ion is ligated by trisamidoamine and three phosphines are left free. Subsequent treatment of **42** with $MnCl_2$ and then KC_8 reduction to produce the diamagnetic quintiply bonded heterodinuclear complex **43** in a very good yield. Interestingly, the Mn atom is ligated by three phosphorus atoms in **43**. As a result, **43** represent the first quintuple bonded species not only containing two different metals, but also two different types of donor atoms. This stepwise synthetic protocol provides a wide scope for assembling various heterobimetallic quintuply bonded complexes in this emerging field.[31]

((Scheme 10))

Up to 2008, the reports of quintuple bonding only were focused on Cr atom and no documents were found on the Mo–Mo quintuple bonds, although a large number of quadruply bonded dimolybdenum complexes have been identified.[2] The first two Mo–Mo quintuple bonded complexes **48** and **49** were reported by Tsai and co-workers upon employment of the monoanionicamidinates as supporting ligands, which have less N−Mo π interactions[27] compared to the previously reported complex **8**.[32] They developed a new synthetic protocol for the synthesis of **48** and **49**, from the quadruply bonded precursors $Mo_2(\mu\text{-}Cl)[Cl_2Li(OEt)][\mu\text{-}\kappa^2\text{-}RC(N\text{-}2,6\text{-}{}^iPr_2C_6H_3)_2]_2$ (R = H (**46**), Ph (**47**)), which were entirely different from the synthesis of the dichromium quintuple bonded complexes. The preparation of **48** and **49** followed the pathway as shown in Scheme 11. A suspension of $K_4Mo_2Cl_8$ in THF was mixed with 2 equiv of lithiated amidinate $Li[RC(N\text{-}2,6\text{-}{}^iPr_2C_6H_3)_2]$(R = H (**44**), Ph (**45**)) and allowed to stir for 72 h at 60 °C, from which two quadruply bonded dimolybdenum complexes **46** and **47** with a paddlewheel configuration were obtained. Compounds **46** and **47** were subsequently reduced by KC_8 in THF to afford the burgundy complexes **48** and **49** in 40% and 16% yield, respectively.[27]

((Scheme 11))

In 2012, Tsai's group reported a new lantern type of Mo–Mo quintuple bonded complex $[Mo_2(\mu\text{-}Li)\{\mu\text{-}CH(N\text{-}2,6\text{-}Et_2C_6H_3)_2\}_3]$ (**53**) in which the Mo–Mo quintuple bond is spanned by one lithium atom in addition to three amidinato ligands. The synthetic pathway is different from that of the previously reported quintuply bonded dimolybdenum complexes **48** and **49**. Over the course of the synthesis, they were able to isolate and characterize an unusual intermediate $[Mo_2\{\mu\text{-}HC\text{-}(N\text{-}2,6\text{-}Et_2C_6H_3\}_2(\mu\text{-}Cl)\{(\mu\text{-}Cl)_2Mo(\mu\text{-}Cl)_2Li(THF)(OEt_2)\}]$ (**51**) (Scheme 12)[29] which was prepared through the reaction of the lithiated amidinate $Li[HC(N\text{-}2,6\text{-}Et_2\text{-}C_6H_3)]$(**50**) with a mixture of $[Mo_2Cl_6\text{-}(THF)_3]$ and Zn powder in THF at −35 °C. Subsequent reduction of **51** with 4 equiv of KC_8 gave **53** in 11% yield. Alternatively, **53** was obtained in 17% yield through KC_8 reduction of the quadruply bonded $[Mo_2\{\mu\text{-}HC(N\text{-}2,6\text{-}Et_2C_6H_3)\}_2(\mu\text{-}Cl)\{(\mu\text{-}Cl)_2Li(THF)_2\}]$ (**52**), which is structurally similar to the previously reported molybdenum complexes **46** and **47**. They emphasized the formation of quintuply bonded dimolybdenum complex **53** in low yields is mainly due to a complicated ligand redistribution process.[29]

((Scheme 12))

Structural characterization and bonding analysis of the quintuple bonded dichromium and dimolybdenum species

In complex **1**, the core two chromium atoms and two *ipso* carbon atoms of the flanking phenyl rings were co-planar and adopt a *trans*-bent configuration with C_{2h} local symmetry. It showed centre of symmetry at the midpoint of the Cr–Cr bond. The Cr–Cr bonding was due to the interaction of two Cr(I) metal centres with a d^5 electronic configuration. It may be argued that in the quintuply bonded complexes, the shortness of metal-metal bond length could be caused by the surrounding sterically encumbering ligands which push the metal atoms to be closer. To compare with the Cr–Cr bond length in **1**, Power et al. Synthesized Ar'MMAr' [M= Fe, Co][36] and **2**-**4** with a metal-metal bond length of 2.5151(9), 2.8033(5) and 1.8077(7), 1.8160(5), 1.831(2) Å, respectively.[34] In light of these longer metal–metal bond lengths, Power implied that the short metal–metal bond length in **1** was mainly due to bonding interactions between two Cr(I) ions instead of the ligand constraint. Furthermore, magnetic measurements on **1**-**4** show temperature-independent weak paramagnetism,[34] consistent with strongly coupled d^5-d^5 bonding electrons. DFT computational studies revealed that the effective bond order of **1** is 3.43.[21] Theoretical investigations indicated the presence of isopropyl groups (${}^iPr$) can further stabilize Ar′CrCrAr′ by 20 kcal/mol compared to the two monomeric Ar′Cr fragments through stabilizing van der Waals dispersion interactions.[37, 38] The Cr–Cr bond length in **1** was significantly longer than those of the N-donor stabilized quintuply bonded complexes.[22-25]

((Fig. 3))

The X-ray molecular structure of **10** depicted in Figure 3 reveals that both Cr atoms are surrounded by three amidinates in a distorted trigonal geometry with N−Cr(1)−N bond angles of 106.96(10), 123.15(11) and 125.53(11)°, and N−Cr(2)−N bond angles of 107.57(10), 126.00(00) and 122.73(11)°. This structural distortion was not due to crystal packing but Jahn-Teller effect, since **10** has a $\sigma^2\pi^4\delta^3$ configuration and the degenerate two δ orbitals are unevenly occupied. Such structural distortion due to Jahn-Teller was for the first time observed in a dinuclear complex. The lantern complex **11** displayed a more symmetrical D_3-symmetry structure with the Cr–Cr bond length of 1.7397(9) Å, which is 0.08 Å shorter compared to its precursor **10**. This was the shortest metal–metal bond length by 2009.[23] Electronically, the Cr–Cr quintuple bond of complex **11** featured a $\sigma^2\pi^4\delta^4$ configuration. DFT calculations (BP86) indicated the effective Cr–Cr bond order of **11** is 4.11.[23]

((Fig. 4))

In the year of 2008, Tsai and co-workers investigated how the Cr–Cr quintuple bond length is affected by steric bulk of the supporting amidinate ligands. They characterized four complexes **16-19** as shown in Figure 4.[24] In complexes **16-18**, the two chromium atoms, the two three-atom N–C–N backbones, and the four carbon atoms of the phenyl rings were completely coplanar. The central Cr_2N_4 core structure of **19** which carried the most sterically hindered amidinate ligands among **16-19**, was not planar with torsion angles of 171.12° (N2–Cr2–Cr1–N3) and 156.05° (C29–N3–Cr1–Cr2) due to inter-ligand steric repulsion between adjacent 2,6-^{i}Pr$_2$C$_6$H$_3$ substituents. The Cr−Cr bond lengths in **16-19** were approximately equivalent at around 1.74 Å. These metric parameters suggested that the Cr−Cr bond lengths of the dichromium bis(amidinato) complexes be irrespective of the steric bulk of amidinate ligands. These results are in sharp contrast to theoretical studies on some of the N-donor-supported quintuple bonded dichromium complexes, revealing that correlation between the CrCr bond length and the effective bond order (EBO) is strongly affected by the nature of the ligand.[39] However, this could be that the variation of the steric bulk of the amidinates in **16-19** is not significant, because Kempe reported that the Cr–Cr quintuple bond length in **30** can be dramatically decreased to 1.71 Å, when the sterically very encumbering guanidinates were employed as supporting ligands. Theoretically optimized structures matched very well with the geometries of complexes **16-19** and the calculated Cr–Cr bond lengths, 1.7216 Å (**16**), 1.7230 Å (**17**), 1.7250 Å (**18**), 1.7188 Å (**19**) were very close to their corresponding experimental values.[24]

((Fig. 5))

The bonding schemes of complexes **16-19** were explained by unrestricted density functional (DFT) calculations (UBP86) and exemplified by the case of **17**. As per calculations, metal–metal bonding could be found through HOMO to HOMO−3, and HOMO−7 (Figure 5). The metal–metal antibonding δ orbitals are shown by LUMO and LUMO+1 (Figure 6), and ligand-based orbitals were observed from HOMO−4 to HOMO−6. HOMO−2 corresponds to the Cr−Cr σ orbital (d_z^2+d_z^2), and both HOMO−3 (d_{xz}+d_{xz}) and HOMO−7 (d_{yz}+d_{yz}) display the Cr−Cr dπ bonding characters. Two Cr−Cr δ bonding interactions are displayed by HOMO (d_{xy}+d_{xy}) and HOMO−1. It is worth noting that HOMO−1 is a side-on sd hybridized δ bond, which is composed of 24.6% s and 75.4% $d_{x^2-y^2}$, oriented such that the main hybrid orbital axes are parallel to one another. In contrary to the significant Cr−N π bonding (HOMO−2) in Theopold's complex **6**, there is no π bonding between Cr atoms and N donors in **17**. As a result, complexes **16-19** have stronger δ bonding and accordingly shorter Cr–Cr bond lengths.[24]

((Fig. 6))

The crystal structure of **23** is presented in Figure 7. The Cr–N$_{amido}$ and Cr–N$_{pyridine}$ bond lengths (1.998(4) and 2.028(4) Å, respectively) are almost equal and very short. Kempe explained the very short Cr–Cr bond length of 1.749(2) Å was mainly due to the spatial arrangement of both N-donor atoms as shown in Figure 8, but not due to the weak coordination of the amido ligands, which resulted in greater interactions between two Cr centres. Theoretical calculations were performed on **23**, and a $\sigma^2\pi^4\delta^4$ configuration is obtained for Cr-based MOs. The two δ MOs are HOMO and HOMO−1, and two π MOs are HOMO−5 and HOMO−6. The σ MO was found at HOMO−2.[25]

((Fig. 7))
((Fig. 8))

The molecular structure of the dichromium complex **37** was depicted in Figure 9. The most prominent structural feature of **37** was the presence of two potassium cations. Presumably, the two pendant amido nitrogen atoms are stabilized by coordination to K^+ ions, so they do not coordinate to Cr centres and consequently weaken the Cr–Cr bond. Tsai et al. demonstrated that the axial ligands weaken the Cr–Cr quintuple bond by identifying two quintuple bonded dichromium amidinates [(THF)Cr(μ-κ^1:κ^1-HC(N-2,6-Me$_2$C$_6$H$_3$)$_2$)]$_2$ (**39**) and {(2-MeTHFCr)Cr[(μ-κ^1:κ^1-HC(N-2,6-Me$_2$C$_6$H$_3$)$_2$)]$_2$} (**40**). Compound **39** features two axial THF ligands, while 40 carries one 2-MeTHF molecule ligating to one Cr atom. Consequently, the Cr–Cr bond length in **39** (1.8115(12) Å) is significantly longer than that (1.7634(5) Å) of **40**, and both are much longer than that (1.7443(10) Å) of **37**. Removal of one potassium ion from **37** by the addition of one equiv of 18-C-6 resulted in complete rupture of the Cr–Cr quintuple bond and gave the mono nuclear chromium complex [(η^3-CH$_3$C$_6$H$_5$)K-@18-C-6][K{μ-η^1:κ^1:η^1:κ^2-2,6-(2,6-^{i}Pr$_2$C$_6$H$_3$-N)$_2$-4-CH$_3$-C$_5$H$_2$N}$_2$Cr] (**38**) in a high yield (Scheme 9).[30] Theoretically, the X-ray data of **37** is in a good agreement with the theoretical calculations at BP86 level. The Cr–Cr bonding formation was rationalized on the basis of five MOs, of which two HOMO−10 (d_{yz}−d_{yz}) and HOMO−6 (d_{xz}−d_{xz}) depicted the Cr–Cr π bonds, while the Cr–Cr σ bond was represented by HOMO−4 (d_z^2+d_z^2). The HOMO and HOMO−1 undoubtedly indicated two Cr–Cr δ bonds (Figure 10).

((Fig. 9))

((Fig. 10))

Based on the so far characterized quintuple bonded dichromium species, those carrying N-donor ligands have much shorter Cr–Cr bond lengths than those with C-donor ligands as shown in Table 1. The origin of such distinction is not clear yet.

It could a consequence of the ligand bridging effect. Tsai and Kempe employed bidentate three-atom bridging ligands to stabilize the quintuple bonded dichromium units, which all show ultrashort Cr−Cr quintuple bonds, particularly, those carry guanidinates **28** and **30**. 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 **6**. 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. However, the electronic effect from ligands cannot be ignored. In light of the stronger σ donation of aryl ligands than amidinates, amidopyridines and a diazadienide, compound **1**-**4** may consequently have weaker Cr−Cr σ bonds than those of the N-donor stabilized quintuple bonded dichromium species.

((Table 1))

Complexes **48** and **49** approximately displayed C_{2h} symmetry due to the coplanarity of the N−C−N backbones, *ipso*-carbon atoms of the phenyl rings. The Mo−Mo bond lengths of **48** and **49** are 2.0187(9) and 2.0157(4) Å, respectively, which are the shortest Mo−Mo bond length yet (Figure 11).[27] It is interesting to note that these bond lengths are shorter than that (2.037(3) Å) of the Cotton's tetragonal dimolybdenum complex $Mo_2(\mu\text{-}\eta^2\text{-}pyNC(O)CH_3)_4$ featuring the record short Mo−Mo quadruple bond length.[40] Moreover, Mo−Mo bond lengths in **48** and **49** are shorter than the theoretically predicted Mo−Mo bond length in a range of 2.03-2.10 Å. Tsai suggested that the Mo−Mo quintuple bond lengths do not associate with the steric bulk of the supporting ligand and the Mo−Mo quintuple bond are mainly due to 1σ, 2π, 2δ bonding interactions between two Mo centers. It is noteworthy that the second δ bond is formed in **48** and **49** upon the reduction of their quadruply bonded precursors (**46** and **47**).

((Fig. 11))

In addition to the lantern dichromium complex **11**, Tsai's group reported a new type of quintuple bonded dimolybdenum complex **53**, where the two Mo atoms are spanned by one lithium atom besides three amidinates. The X-ray crystal structure of **53** is shown in Figure 12. The Mo−Mo bond length of **53** is 2.0612(4) Å, longer than that (2.02 Å) of the previously reported quintuply bonded dimolybdenum compounds **48** and **49**.[27] However, it is slightly shorter than the computed bond length (2.070 Å). Like those quintuple bonded group VI metal amidinate dimers, DFT calculations indicated that there were no significant N−Mo π- bonding interactions. The Mo−Mo bonding character of **53** was justified by the nine highest-energy occupied molecular orbitals, namely, from the HOMO down to HOMO−8. Among these nine MOs, HOMO, HOMO−1, HOMO−3, HOMO−7, and HOMO−8 have their electron densities concentrated on the metal centres rather than on the ligands, resulting in metal−metal bonding. On the other hand, HOMO−2, HOMO−4, HOMO−5 and HOMO−6 have most of their electron densities residing on ligands and cause metal−ligand bonding. Among these five occupied Mo−Mo bonding MOs, the Mo−Mo σ character was found at HOMO−3, while HOMO−7 (d_{xz}+d_{xz}) and HOMO−8 (d_{yz}+d_{yz}) represented two Mo−Mo π bonds. As sown in Figure 12, the HOMO ($sd_{x^2-y^2}$+ $sd_{x^2-y^2}$) and HOMO−1 (d_{xy}+d_{xy}) displayed two δ bonds. Considerable electron density was observed between the region of Li ion and the two Mo atoms in HOMO suggesting that the interaction between Li ion and Mo atoms be ionic. HOMO was mainly composed of Li (11.63%) and two Mo (44% from each) atoms based on NBO calculations.[29]

((Fig. 12))

Reactivity of dichromium and dimolybdinum quintuple bonded complexes

Theoretical calculations revealed the Cr−Cr quintuple bond strength of ca. 76 kcal/mole on the basis of a model compound PhCrCrPh,[41] much smaller than that of N≡N (226 kcal/mol) and C≡C (200 kcal/mol) (alkynes) bonds. Considering the characterization of a number of the quintuple bonded species with ultrashort metal-metal separations,[21-30, 33] chemists were then curious about the quintuple bond reactivity. This curiosity was mainly due to their univalent and coordinatively unsaturated dimetal centres. Moreover, these dinuclear quintuple bonded complexes can lose two to eight electrons from the dimetal units and the surrounding steric bulk of ligands at the metal centers only allow the access of small molecules. Preliminary reaction chemistry of these remarkable complexes towards unsaturated molecules (alkenes and alkynes) along with small inorganic molecules was recently reported. Power and co-workers demonstrated the reactions of **1** with heterocumulene reagents, such as an excess of nitrous oxide and one equiv of 1-adamantyl azide (1-AdN$_3$), resulted in the formation of dichromium oxide $Ar'Cr(\mu\text{-}O)_2Cr(O)Ar'$ (**54**) and $Ar'Cr(\mu{:}\kappa^1,\kappa^3\text{-}N_3(1\text{-}Ad))CrAr'$ (**55**) (Scheme 13), respectively.[42] In both **54** and **55**, the Cr−Cr quintuple bonds were completely cleaved. In **54**, the two Cr centres were bridged by two oxygen atoms, one CrAr' unit featured a terminal oxygen atom, and the quintuple bonded Cr_2^{2+} was accordingly oxidized to give a mixed-valent [Cr(III)/Cr(V)] compound **54**. However, in the case of **55**, the azido motif was inserted between the two chromium atoms and resulted in the homodivalent [Cr(II)/Cr(II)] species **55**. Compared to **54** with higher valent Cr centres, **55** may be subsequently treated with more 1-adamantyl azide to generate products with higher valent Cr centres. This result was in contrast with the reaction of the mono valent chromium β-diketiminates with organic azides giving the mononuclear bis(imido) complexes $(RN)_2Cr(HC[C(CH_3)N\text{-}2,6\text{-}{}^iPr_2C_6H_3]_2)$.[43]

((Scheme 13))

Initially, it was assumed that the Cr−Cr quintuple bonds were very different when compared to the carbon-carbon multiple bonds in terms of their reactivity. However, this is not the case. Some parallels between these multiple bonded systems were disclosed. Such studies were initiated by Kempe's group, who employed **24** to activate small molecules due to the controlled steric hindrance on pyridine rings. In 2009, Kempe and co-workers described the carboalumination reaction of **24**.[26] Carbometalation, particularly the carboalumination of carbon-carbon triple and double bonds, is very common in organometallic chemistry and organic synthesis. In general, the addition of trimethylaluminium to C≡C and C=C bonds requires a transition metal complex as catalyst, but a similar reaction to the Cr–Cr quintuple bond of **24** proceeded under catalyst-free conditions.[26] Addition of $AlMe_3$ to **24** yielded the brown diamagnetic carboalumination adduct $[Cr(\mu\text{-}Ar)]_2(\mu\text{-}CH_3)(\mu\text{-}AlMe_2)$ [Ar = 2-(N-2,6-$Me_2C_6H_3$)-6-(2,6-$^iPr_2C_6H_3$)-C_5H_3N] (**56**) in 92% yield, in which the Cr–Cr quintuple bond was inserted into one of the three aluminium-carbon bonds (Scheme 14). It is interesting to note that the core structure of **56** displayed an *anti*-configuration, which is in contrast to the addition of trimethylaluminium to the alkenes and alkynes where the addition proceeds via *syn*- and *cis*-addition, respectively.[44, 45] The Cr−Cr bond length of **56** is 1.8365(8) Å, an "ultrashort" Cr–Cr quadruple bond.[26]

Although the chromium oxo complexes were first reported by Herberhold,[46] they are still scarce. To gain more insight into these species, Kempe and co-workers prepared dinuclear chromium oxo compounds based on the highly reducing nature of **24**. Exposure of **24** to molecular oxygen resulted in the isolation of the diamagnetic chromium dioxo dimer $[CrArO(\mu\text{-}O)]_2$ (**57**) (Ar = 2-(N-2,6-$Me_2C_6H_3$)-6-(2,6-$^iPr_2C_6H_3$)-C_5H_3N).[26] The structure of **57** featured two oxygen atoms coordinated to two Cr atoms in a bridging mode and two oxo ligands terminally ligated the Cr centers, which is different from the previously reported mononuclear chromium (V) dioxo stabilized by a bulky β-diketiminate ligand (Scheme 14).[43] The long separation between the two Cr centres of 2.5314(10) Å in **57** is indicative of a single bond between two Cr atoms.

((Scheme 14))

Inspired by the reaction chemistry of **24** with O_2, Kempe and co-workers extended the same principle to the heavier congeners of oxygen. In contrast to the strong oxidizing ability of O_2, reactions of **24** and respective elemental sulfur, selenium and tellurium do not produce terminal chalcogenides. Compounds $[Cr\text{-}(\mu\text{-}\kappa^2\text{-}Ar)]_2[\mu\text{-}\kappa^2\text{-}\kappa^2\text{-}E_2]$ (Ar = 2-(N-2,6-$Me_2C_6H_3$)-6-(2,6-$^iPr_2C_6H_3$)-C_5H_3N), $E_2 = S_2$ (**58**), Se_2 (**59**), Te_2 (**60**)) were instead obtained, in which two Cr centres are respectively ligated by a disulphide, deselenide and detelluride, and the oxidation state of each Cr is II (Scheme 14).[47] The Cr−Cr bond lengths of **58** and **60** are 1.847(2) and 1.8369(18) Å, respectively, typical for the Cr–Cr quadruple bond. Furthermore, Kempe et al. explored the reaction chemistry of **24** with halogens to give $[Cr\text{-}(\mu\text{-}\kappa^2\text{-}Ar)]_2(\mu\text{-}X)_2$ (Ar = 2-(N-2,6-$Me_2C_6H_3$)-6-(2,6-$^iPr_2C_6H_3$)-C_5H_3N), X = Cl (**61**), Br (**62**), I (**63**))[47] which are different from Power's complex **1**, where the quintuple bonded Cr_2^{2+} unit was completely oxidized and split into the mononuclear Cr(II) species $[CrI_2(THF)_2]$.[48] Such reactivity difference is presumably due to the chelating ligands of **24**, holding two Cr atoms together. Moreover, **24** activated the diphenyldichalcogenides Ph_2E_2 (E = S, Se) to give rise to the formation of $[Cr\text{-}(\mu\text{-}\kappa^2\text{-}Ar]_2[\mu\text{-}\kappa^2\text{-}\kappa^2\text{-}EPh]$ (Ar = 2-(N-2,6-$Me_2C_6H_3$)-6-(2,6-$^iPr_2C_6H_3$)-C_5H_3N) and E = S (**64**), Se (**65**)) (Scheme 14).[47] The central cores Cr_2X_2 of **61**, **62** and **63** displayed a diamond shape, while the corresponding Cr_2E_2 in **64** and **65** exhibited a butterfly configuration. In complexes **61**-**65**, all Cr–Cr bond lengths (from 1.8486(19) to 1.918(12) Å) are in the range of Cr–Cr quadruple bonds.[47]

Activation of white phosphorous by main group elements[49] and transition metals[50-52] has been well documented. Few reports are available on bimetallic activation of P_4 by dinuclear transition metal systems, only through stepwise construction.[53-57] Although the quintuple bonded Cr_2 centres can lose up to eight electrons, they usually donate two electrons and keep quadruple bonding character upon reacting with less oxidizing substrates. In 2011, Kempe and co-workers demonstrated that the bimetallic activation of the Cr–Cr quintuple bond not only with P_4 molecule but also with AsP_3 and As_4 molecules resulted in the formation of the E_4-coordinated ($E_4 = P_4$, AsP_3, As_4) dichromiumadducts.[58] As shown in Scheme 14, the reactions of **24** with P_4, As_4 and AsP_3 in THF gave $[Cr\text{-}(\mu\text{-}\kappa^2\text{-}Ar)]_2[\mu_3\text{-}\kappa^1\text{-}\kappa^3\text{-}\kappa^3\text{-}E_4]$ (Ar = 2-(N-2,6-$Me_2C_6H_3$)-6-(2,6-$^iPr_2C_6H_3$)-C_5H_3N, $E_4 = P_4$ (**66**), As_4 (**67**), AsP_3(**68**)).[58] The E_4 groups in **66**-**68** displayed a nearly square planar geometry and short Cr–Cr quadruple bond lengths of 1.8664(8), 1.863(2), and 1.8735(5) Å, respectively. Both P−P and As−As bond lengths in **66** and **67** are shorter than the normal P−P and As−As bonds. It is worth noting that the lone pair on each atom of the formed *cyclo*-E_4^{2-} units is active, which further reacted with an excess amount of $[W(CO)_5(THF)]$ to give the mono-substituted product $[Cr\text{-}(\mu\text{-}\kappa^2\text{-}Ar)]_2[\mu_3\text{-}\kappa^1\text{-}\kappa^3\text{-}\kappa^3\text{-}P_4][W(CO)_5]$ (**69**). Kempe et al. suggested that the exclusive formation of **69** be mainly due to steric congestion of the molecule of **66**.

Low-valent and low-coordinate complexes form adducts with alkynes and dienes. For example, Rosenthal, Erker, Beckhaus, and Mach have used dienes and alkynes as protecting ligands for low-valent group IV metallocenes.[59-81] In light of the univalent and coordinatively unsaturated Cr atoms in the quintuple bonded dichromium complexes, the question is to what extent the quintuple bonded species can participate in cycloaddition reactions, which are analogous to carbon-carbon multiple bonds. To this end, Kempe and co-workers demonstrated [2+2] cycloaddition reactions of the quintuply bonded dichromium species **24** and substituted acetylenes and dienes (Scheme 14).[82] They synthesized $[Cr(\mu\text{-}Ar)]_2[(\mu\text{-}\kappa^2\text{-}RCCR')]$(R = R' = Ph (**70**), R = H, R' = Ph (**71**); R = H, R' = $Si(CH_3)_3$ (**72**); R = H, R' = C_6H_4-*p*-CH_3 (**73**)) upon addition of **24** to diphenylacetylene, phenylacetylene, trimethylsilylacetylene and p-tolylacetylene, respectively.[82] Interestingly, no reaction was observed between bis(trimethylsilyl)acetylene and **24**, presumably due to steric issue. Their structure of these four adducts was confirmed by the crystal structure determination of **73**, which carried a very short Cr–Cr quadruple bond of 1.8041(15) Å. It is noteworthy that **24** also served as a dienophile, undergoing a Diels-Alder-like [4+2] reaction with a conjugated olefin. Kempe and co-workers characterized the adducts $[Cr(\mu\text{-}Ar)]_2[\mu\text{-}\kappa^3\text{-}CH_2CRCHCH_2]$ (R = CH_3 (**74**), H (**75**)) from the reactions of buta-1,3-diene and 2-methylbutadiene with **24**, respectively.[82] Complexes **70**-**75** showed that both dienes and alkynes preferably coordinate to the top of the chromium atoms by folding the two aminopyridinato ligand away from metals. Both bond orders in **74** and **75** were reduced and their bond lengths of **74** (1.8228(8)Å) and **75**

(1.8227(14) Å) are longer than that of **24**, but are in the "supershort" quadruple bond range as well.[2] It is of surprise that no reaction was observed when **24** was exposed to 1 bar of ethylene, even though the reaction was stirred at 80 °C for overnight (Scheme 14).

Akin to Kempe's complexation adducts **70**-73 via [2+2] cycloaddition,[82] Theopold and co-workers found similar results based on **6** with internal alkynes. In a diethyl ether solution, reactions of **6** with 2-butyne, 3-hexyne and diphenylacetylene, respectively, elicited an immediate color change from green to deep purple and yielded the complexation adducts [μ-κ^2-HC(N-2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$Cr]$_2$(μ-κ^2-RCCR) (R = Me (**76**), Et (**77**), Ph (**78**)). (Scheme 15) The Cr–Cr bond lengths in **76**, **77** and **78** are 1.9248(7), 1.9361(7) and 1.9186(7) Å, respectively, falling into the range of Cr–Cr quadruple bonds. The formal oxidation state of Cr in **76**-**78** is 2+. As a result, compound **6** chemically features a Cr–Cr quintuple bond.[83] Similarly, they did not observe further reactions of **76**-**78** with an excess amount of alkynes.[84] To facilitate the electron flow from the quintuple bonded Cr$_2$ unit to an alkyne molecule, Theopold and co-workers conducted an experiment of **6** with an electron-deficient alkyne. Addition of **6** to an excess of hexafluoro-2-butyne resulted in the isolation of an intermediate **79**, in which the alkyne was not only added across the Cr$_2$ unit, but also a Cr-ligand moiety to generate a new ligand iminoamide (Scheme 15).[84]

((Scheme 15))

The cycloaddition is one important reaction of organic molecules containing carbon–carbon multiple bonds, leading to the synthesis of various substituted aromatics. For example, the [2+2+2] cyclotrimerization of acetylenes catalyzed by transition metal complexes have been well documented.[85-89] Tsai and co-workers recently reported a similar reaction based on the Mo–Mo quintuple bonded amidinates. They showed that **48** and **49** underwent the catalyst-free [2+2+2] cycloaddition reactions with terminal alkynes to generate novel aromatics containing a multiple bonded dimolybdenum unit.[90] As illustrated in Scheme 16, reactions of **48** in THF and **49** in diethyl ether with two equivalent of 1-pentyne at room temperature afforded the diamagnetic [2+2+2] products [Mo$_2$(μ-κ^1:κ^1-1,3-^{n}Pr$_2$C$_4$H$_2$){μ-κ^2-RC(N-2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$}$_2$] (R = H (**80**), Ph (**81**)) which were isolated in 60 and 67% yield, respectively. The most salient structural feature of **80** and **81** is the aromatic Mo$_2$C$_4$ metalacycles with two ^{n}Pr substituents on the same face of the rings due to the steric repulsions between the bulky ^{i}Pr substituents of amidinates and ^{n}Pr substituents. On the other hand, treatment of **48** and **49** with 2 equiv of 3-hexyne exclusively yielded the diamagnetic [2+2] complexation adducts Mo$_2$(H)(μ-κ^2:κ^2-EtCCEt)$_2$[κ^2-HC(N-2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$][κ^3-HC(N-2,6-^{i}Pr$_2$C$_6$H$_3$)-(N-2-CH(CH$_2$)CH$_3$-6-^{i}Pr-C$_6$H$_3$)] (**82**) and [Mo$_2$(μ-κ^2-EtCCEt)$_2${μ-κ^2-PhC(N-2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$}$_2$] (**83**), respectively.[90] The formation of **82** and **83** is presumably due to the different steric pressure of the ligands, since **48** features two less bulky amidinates than **49**, and, consequently, can accommodate two alkynes. Upon double alkyne complexation of **48**, the Mo centres became electron rich to undergo intramolecular C-H activation to give **82**. They further examined the reactions of the quintuply bonded dichromium complex **18** with internal and terminal alkynes. However, the [2+2] cycloaddition compounds [Cr$_2$(μ-κ^2-R^{2}CCR^3)$_2${μ-κ^2-HC-(N-2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$}$_2$] (R^2 = H, R^3 = ^{n}Pr (**84**), R^2 = R^3 = Et (**85**), R^2 = R^3 = Ph (**86**)) are the only isolated products. It is worthy to note that **84-86** exhibit a similar structural configuration, where the bridging alkyne ligands are skewed with respect to the metal-metal bond axes.[90] Compounds **80** and **81** are the first two examples of 1,2-quadraply bonded dimolybdenum benzene derivatives, which consists of a six-electron six-center d$_\delta$-p$_\pi$ conjugation system with a metal-metal δ bonding.[90]

((Scheme 16))

During the preparation of this manuscript, Tsai and co-workers reported another carbon-carbon multiple bond-like reaction chemistry of the quintuple bonded dichromium and dimolybdenum amidinate complexes (**18** and **48**). Promoted by Lewis acids, addition of acyl chlorides to alkynes leading to β-chloro α,β-unsaturated ketones is well known in organic chemistry.[91] These compounds are very important precursors to the synthesis of many organic substrates mainly N- and O-containing heterocycles, which are very useful in chemical and pharmaceutical industries.[91, 92] Similar to the preparation of β-chloro α,β-unsaturated ketones, Tsai et al. demonstrated **48** undergo facile haloacylation (or oxidative addition) reactions upon treatment with acyl halides to give β-halo α,β-quadruple-bonded dimolybdenum acyl complexes *anti*-Mo$_2$(X)(μ-κ^2-OCR)[μ-κ^2-HC(N-2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$]$_2$ (R = C$_6$H$_5$, X = Cl (**87**), R = C$_6$H$_5$, X = Br (**88**), R = 2-MeC$_6$H$_4$, X = Cl (**89**), R = Me, X= Cl (**90**)) under catalyst-free conditions (Scheme 17). These reactions proceeded fast in regular hydrocarbon solvents. Similarly, **18** also underwent haloacylation with acid halide to give *anti*-Cr$_2$(μ-Cl)(μ-κ^2-OC-2-Me-C$_6$H$_4$)[μ-κ^2-HC(N-2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$]$_2$ (**91**). Compound **91** features a bridging chloro ligand, which is slightly different from **87-90**, where the halides are terminally ligated. These haloacylation products represent the first examples of Friedel-Crafts type of haloacylation of the metal–metal multiple bonds. Interestingly, complexes **87-90** further reacted with another equivalent of acyl halides to give rise to the formation of bridging carbine dimolybdenum complexes [Mo$_2$(X)(μ-X')(μ-CR^1)(κ^2-O$_2$CR^2){μ-κ^2-HC(N-2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$}$_2$](R^1= R^2= C$_6$H$_5$, X= X' = Cl (**92**), R^1= R^2= C$_6$H$_5$, X = X' = Br (**93**), R^1= R^2= 2-MeC$_6$H$_4$, X = X' = Cl (**94**), R^1= R^2= CH$_3$, X = X' = Cl (**95**), R^1= C$_6$H$_5$, R^2= 2-MeC$_6$H$_4$, X = X' = Cl (**96**), R^1= 2-MeC$_6$H$_4$, R^2= C$_6$H$_5$, X = X' = Cl (**97**)), which feature a carboxylato and two halo ligands in addition to two bridging amidinates via acyl disproportionation. The authors concluded that the carbyne ligands were derived from the first acyl groups after examining reactions of **48** with various acyl halides.[93] In addition, both bridging and terminal halo ligands in **92-97** are labile; they underwent an intramolecular swap and intermolecular exchange. This protocol provides a facile pathway to synthesize metal carbynes.

((Scheme 17))

Given that the Cr–Cr and Mo–Mo quintuple bonds have a potential to undergo organic-like cycloaddition and haloacylation reactions along with activation of the group 15-17 elements, Tsai and his group turned their attention to the activation of nitric oxide. Several bimetallic nitrosyl complexes were notified, but no reports received by the direct reaction of dinuclear complexes with nitric oxide.[94] For the first time, Tsai and co-workers showed nitric oxide activation by the univalent quintuply bonded Cr and Mo amidinates.[95] As illustrated in Scheme 18, **17** reacted with an excess amount of nitric oxide at −78 °C to result in the isolation of the mononuclear dinitrosyl $Cr(NO)_2[\kappa^2\text{-}HC(N\text{-}2,6\text{-}Et_2C_6H_3)_2]_2$ (**98**) and dinuclear species $Cr_2(\mu\text{-}\kappa^1\text{-}ONO)_2(NO)_4[\mu\text{-}\kappa^2\text{-}HC(N\text{-}2,6\text{-}Et_2C_6H_3)_2]_2$ (**99**). On the contrary, if the reaction was carried out at room temperature, the only identifiable product was **98**. Interestingly, **99** is not transformed into **98** upon warming. These results imply the highly reactive nature of **17**, which carries two small amidinato ligands. For comparison, they also conducted the same experiments with the Mo–Mo quintuple bonds. The reactions of **18** and **49** with an excess amount of NO in THF at −78 °C led to the isolation of the diamagnetic nitrito products $(\kappa^2\text{-}NO_2)\text{-}Cr(\mu\text{-}NO)_2[\mu\text{-}\kappa^2\text{-}HC(N\text{-}2,6\text{-}{}^iPr_2C_6H_3)_2]_2CrNO$ (**100**) and *cis*-$Mo_2[\mu\text{-}\kappa^1\text{:}\kappa^1\text{-}NO_2]_2[\mu\text{-}\kappa^2\text{-}PhC(N\text{-}2,6\text{-}{}^iPr_2C_6H_3)_2]_2$ (**101**). Complex **100** exhibits an unsymmetrical structural configuration with two different metal centres, whereas **101** adopts a symmetrical paddlewheel configuration, whereby the two nitrito groups in **101** are arranged in an unexpected *cis*-configuration concomitant with two sterically hindered amidinates. The bond length between two Mo atoms is 2.0857(4) Å, typical of a Mo–Mo quadruple bond. These studies suggested that the bonding between two Mo atoms is stronger than that of the two Cr atoms[95] and the NO activation can be accomplished by low-valent dinuclear complexes in addition to mononuclear transition metal species.

((Scheme 18))

Concluding Remarks

Initiated by theoretical works, research in the quintuple bonding has significantly grown in particularity since the landmark discovery of Power's quintuple bonded chromium phenyl dimer **1**.[21] The follow-up utilization of bulky bidentate ligands has allowed the isolation of a number of quintuple bonded group VI metal dimers. Although the quintuple bonded species can exist with various configurations on the basis of theoretical calculations,[96] three types of geometries have so far been recognized, and the type II compounds predominate in this field. Such discrepancy is due to the difference in steric hindrance of the supporting ligands employed in theoretical and experimental studies. Regardless of their structural conformations, all the identified quintuple bonded complexes have ultrashort metal-metal distances. Furthermore, these very short metal-metal quintuple bond lengths show slight dependence on the bulk of the supporting ligands, although the shortest metal-metal bond lengths were found in the chromium guanidinate dimers **28**[28] and **30**,[33] featuring the most sterically encumbering ligands among the characterized quintuple bonded compounds. Besides, more attentions should be paid to the lantern type III complexes, in which many of the metal valence orbitals participate in σ bonding to the ligands, because compound **11** has an unexpectedly ultrashort Cr–Cr bond length.[23] Moreover, the remarkable type III heterodinuclear Cr–Mn complex **43**[31] not only features a very short Cr–Mn quintuple bond, but also represents a milestone in the construction of the quintuple bonded dinuclear compounds beyond the group VI metals.

Quintuple bonding is still in its infancy, compared with the well-developed quadruple bonding. The thus far characterized quintuple bonded dinuclear complexes are mainly on Cr and Mo. Characterizing more compounds containing quintuple bonded bimetal units will definitely help the chemists gain more insight into this field. Accordingly, tungsten,[98] a heavier congener of Cr and Mo, has been the next target. Other than the group VI metal elements, the heavy transition metal elements, rhenium,[97, 98] osmium,[98] and niobium[13, 99] and actinium elements, uranium[100, 101] and protactinium,[101] have been theoretically predicted to be capable of forming quintuply bonded dimeric compounds. King et al, reported the hypothetical organometallic molecules $Cp_2Re_2(CO)$,[97] bent dimetallocenes Cp_2M_2 (M = W, Re, Os),[98] and $Nb_2(CO)_8$[99] feature the metal-metal quintuple bonds based on the 18-electron rule. Moreover, the Nb_2 molecule has been experimentally probed and predicted to have a strong quintuple bond, consistent with its electronic configuration of $4d^45s^1$.[13] The simple diactinide molecules Pa_2[100] and U_2[99, 100] were also suggested to have the metal-metal quintuple bonds by Gagliardi et al. However, it is challenging to structurally characterize these quintuple bonded diatomic molecules unless they can be stabilized by neutral ligands, like the diboryne stabilized by two bulky N-heterocyclic carbenes.[102]

Preliminary reactivity studies indicate that these low-valent and low-coordinate quintuple bonded dinuclear complexes are highly reducing and reactive towards small molecules, such as chalcogens, pnictogens, nitric oxide and unsaturated olefins. Of particular interest is that they, particularly the Mo–Mo quintuple bonded amidinates, show analogous reactivity to that of the π-system alkynes and olefins in some ways. The chemistry of molecules containing carbon-carbon multiple bonds have been studied for more than two centuries; more efforts are needed to explore the newly born complexes containing metal-metal quintuple bonds.

Acknowledgements

We are grateful to the numerous co-workers who have contributed to our papers reviewed in this article. The support from 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 is also gratefully acknowledged.

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**, 762-785.
2. F. A. Cotton, C. A. Murillo and R. A. Walton, *Multiple Bonds Between Metal Atoms*, Springer, Berlin, 3rd Ed, 2005.

3. J. A. Bertrand, F. A. Cotton and W. A. Dollase, *J. Am. Chem. Soc.*, 1963, **85**, 1349-1350.
4. *idem.*, *Inorg. Chem*. 1963, **2**, 1166.
5. W. I. Robinson, J. E. Fergusson and B. R. Penfold, *Proc. Chem. Soc.,* 1963, 116.
6. A. Werner, *Neuere Anschauungen auf dem Gebiete der anorganischen Chemie*, Braunschweig, 1905.
7. P. Pfeiffer, *in Great Chemists*, ed. E. Farber, Interscience, New York, 1961, p. 1233.
8. G. B. Kauffman, *Coord. Chem. Rev.*, 1973, **11**, 161-188.
9. G. B. Kauffman, *Coord. Chem. Rev.*, 1974, **12**, 105-149.
10. G. B. Kauffman, *Coord. Chem. Rev.*, 1975, **15**, 1-92.
11. G. B. Kauffman, *Coord. Chem. Rev.*, 1973, **9**, 339-363.
12. F. A. Cotton, N. F. Curtis, C. B. Harris, B. F. G. Johnson, S. J. Lippard, J. T. Mague, W. R. Robinson and J. S. Wood, *Science*, 1964, **145**, 1305-1307.
13. W. Klotzbuecher and G. A. Ozin, *Inorg. Chem.*, 1977, **16**, 984-987.
14. S. K. Gupta, R. M. Atkins and K. A. Gingerich, *Inorg. Chem.*, 1978, **17**, 3211-3213.
15. M. D. Morse, *Chem. Rev.*, 1986, **86**, 1049-1109.
16. S. M. Casey, P. W. Villalta, A. A. Bengali, C. L. Cheng, J. P. Dick, P. T. Fenn and D. G. Leopold, *J. Am. Chem. Soc.*, 1991, **113**, 6688-6689.
17. M. H. Chisholm and A. M. Macintosh, *Chem. Rev.*, 2005, **105**, 2949-2976.
18. A. Dedieu, T. A. Albright and R. Hoffmann, *J. Am. Chem. Soc.*, 1979, **101**, 3141-3151.
19. F. Weinhold and C. R. Landis, *Chem. Ed. Res. Pract.*, 2001, **2**, 91-104.
20. F. Weinhold, C. R. Landis, *Valency and Bonding: A Natural Bond Orbital Donor-Acceptor Perspective*, Cambridge Univer-sity Press, Cambridge, 2005, 555-559.
21. T. Nguyen, A. D. Sutton, M. Brynda, J. C. Fettinger, G. J. Long and P. P. Power, *Science*, 2005, **310**, 844-847.
22. K. A. Kreisel, G. P. A. Yap, O. Dmitrenko, C. R. Landis and K. H. Theopold, *J. Am. Chem. Soc.*, 2007, **129**, 14162-14163.
23. 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**, 7250-7253.
24. 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**, 9933-9936.
25. A. Noor, F. R. Wagner and R. Kempe, *Angew. Chem. Int. Ed.*, 2008, **47**, 7246-7249.
26. A. Noor, G. Glatz, R. Müller, M. Kaupp, S. Demeshko and R. Kempe, *Nat. Chem*, 2009, **1**, 322-325.
27. 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**, 12534-12535.
28. A. Noor, G. Glatz, R. Müller, M. Kaupp, S. Demeshko and R. Kempe, *Z. Anorg. Allg. Chem.*, 2009, **635**, 1149-1152.
29. S.-C. Liu, W.-L. Ke, J.-S. K. Yu, T.-S. Kuo and Y.-C. Tsai, *Angew. Chem. Int. Ed.*, 2012, **51**, 6394-6397.
30. 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**, 7781-7785.
31. 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**, 13142-13148.
32. Y.-C. Tsai, Y.-M. Lin, J.-S. K. Yu and J.-K. Hwang, *J. Am. Chem. Soc.*, 2006, **128**, 13980-13981.
33. A. Noor, T. Bauer, T. K. Todorova, B. Weber, L. Gagliardi and R. Kempe, *Chem. Eur. J.*, 2013, **19**, 9825-9832.
34. 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**, 11277-11290.
35. P. A. Rudd, S. Liu, N. Planas, E. Bill, L. Gagliardi and C. C. Lu, *Angew. Chem. Int. Ed.*, 2013, **52**, 4449-4452.
36. T. Nguyen, W. A. Merrill, C. Ni, H. Lei, J. C. Fettinger, B. D. Ellis, G. J. Long, M. Brynda and P. P. Power, *Angew. Chem. Int. Ed.*, 2008, **47**, 9115-9117.
37. S. Ndambuki and T. Ziegler, *Inorg. Chem.*, 2012, **51**, 7794-7800.
38. S. Ndambuki and T. Ziegler, *Inorg.Chem.*, 2013, **52**, 3860-3869.
39. G. La Macchia, G. Li Manni, T. K. Todorova, M. Brynda, F. Aquilante, B. O. Roos and L. Gagliardi, *Inorg.Chem.*, 2010, **49**, 5216-5222.
40. F. A. Cotton, L. M. Daniels, E. A. Hillard and C. A. Murillo, *Inorg.Chem.*, 2002, **41**, 2466-2470.
41. M. Brynda, L. Gagliardi, P.-O. Widmark, P. P. Power and B. O. Roos, *Angew. Chem. Int. Ed.*, 2006, **45**, 3804-3807.
42. C. Ni, B. D. Ellis, G. J. Long and P. P. Power, *Chem. Commun.*, 2009, 2332-2334.
43. Y.-C. Tsai, P.-Y. Wang, S.-A. Chen and J.-M. Chen, *J. Am. Chem. Soc.*, 2007, **129**, 8066-8067.
44. Elschenbroich, Ch.*Organometallchemie* 5th Ed Teubner, 2005.
45. A. G. Fallis and P. Forgione, *Tetrahedron*, 2001, **57**, 5899-5913.
46. M. Herberhold, W. Kremnitz, A. Razavi, H. Schöllhorn and U. Thewalt, *Angew. Chem. Int. Ed.*, 1985, **24**, 601-602.
47. E. S. Tamne, A. Noor, S. Qayyum, T. Bauer and R. Kempe, *Inorg.Chem.*, 2012, **52**, 329-336.
48. C. Ni, P. P. Power., *Struct. Bonding* (Berlin, Germany) 2010, 136, 59-112.
49. M. Scheer, G. Balázs and A. Seitz, *Chem. Rev.*, 2010, **110**, 4236-4256.
50. M. Caporali, L. Gonsalvi, A. Rossin and M. Peruzzini, *Chem. Rev.*, 2010, **110**, 4178-4235.
51. B. M. Cossairt, N. A. Piro and C. C. Cummins, *Chem. Rev.*, 2010, **110**, 4164-4177.
52. M. Peruzzini, L. Gonsalvi and A. Romerosa, *Chem. Soc. Rev.*, 2005, **34**, 1038-1047.
53. M. Peruzzini, L. Marvelli, A. Romerosa, R. Rossi, F. Vizza and F. Zanobini, *Eur. J. Inorg. Chem.*, 1999, 931-933.
54. P. Barbaro, M. Di Vaira, M. Peruzzini, S. Seniori Costantini and P. Stoppioni, *Chem. Eur. J.*, 2007, **13**, 6682-6690.
55. M. Caporali, M. Di Vaira, M. Peruzzini, S. Seniori Costantini, P. Stoppioni and F. Zanobini, *Eur. J. Inorg. Chem.*, 2010, 152-158.
56. D. Yakhvarov, P. Barbaro, L. Gonsalvi, S. Mañas Carpio, S. Midollini, A. Orlandini, M. Peruzzini, O. Sinyashin and F. Zanobini, *Angew. Chem. Int. Ed.*, 2006, **45**, 4182-4185.
57. P. M. Di Vaira and S. S. C. Frediani, M. Peruzzini, P. Stoppioni, *Acta Crystallogr. Sect. A* 2005,**61***,* c298.
58. 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**, 7283-7286.
59. U. Rosenthal, V. V. Burlakov in Titanium and Zirconium in *Org. Synth.* (Ed. : I. Marek), Wiley-VCH, Weinhiemk, 2002, 355–389.
60. U. Rosenthal, V. V. Burlakov, P. Arndt, W. Baumann and A. Spannenberg, *Organometallics*, 2003, **22**, 884-900.
61. U. Rosenthal, Vladimir V. Burlakov, P. Arndt, W. Baumann, A. Spannenberg and Vladimir B. Shur, *Eur. J. Inorg. Chem.*, 2004, 4739-4749.
62. U. Rosenthal, V. V. Burlakov, M. A. Bach and T. Beweries, *Chem. Soc. Rev.*, 2007, **36**, 719-728.
63. U. Rosenthal, P.-M. Pellny, F. G. Kirchbauer and V. V. Burlakov, *Acc. Chem. Res*., 2000, **33**, 119-129.
64. G. Erker, G. Kehr and R. Fröhlich, *J. Organomet. Chem.*, 2004, **689**, 4305-4318.
65. G. Erker, G. Kehr and R. Fröhlich, *Coord. Chem. Rev.*, 2006, **250**, 36-46.
66. G. Erker, G. Kehr and R. FrÖHlich, in *Advances in Organomet. Chem.*, eds. W. Robert and F. H. Anthony, Academic Press, 2004, vol. Volume 51, pp. 109-162.
67. G. Erker, *Chem. Commun.*, 2003, 1469-1476.
68. G. Erker, *Acc. Chem. Res*., 2001, **34**, 309-317.
69. G. Erker, C. Krüger and G. Müller, in *Advances in Organomet. Chem.*, eds. F. G. A. Stone and W. Robert, Academic Press, 1985, vol. 24, pp. 1-39.
70. M. Lamač, A. Spannenberg, H. Jiao, S. Hansen, W. Baumann, P. Arndt and U. Rosenthal, *Angew. Chem. Int. Ed.*, 2010, **49**, 2937-2940.

71. P.-M. Pellny, F. G. Kirchbauer, V. V. Burlakov, W. Baumann, A. Spannenberg and U. Rosenthal, *J. Am. Chem. Soc.*, 1999, **121**, 8313-8323.
72. A. Ohff, P. Kosse, W. Baumann, A. Tillack, R. Kempe, H. Goerls, V. V. Burlakov and U. Rosenthal, *J. Am. Chem. Soc.*, 1995, **117**, 10399-10400.
73. J. Karl, G. Erker and R. Fröhlich, *J. Am. Chem. Soc.*, 1997, **119**, 11165-11173.
74. B. Temme, G. Erker, J. Karl, H. Luftmann, R. Fröhlich and S. Kotila, *Angew. Chem. Int. Ed.*, 1995, **34**, 1755-1757.
75. G. Erker, J. Wicher, K. Engel, F. Rosenfeldt, W. Dietrich and C. Krueger, *J. Am. Chem. Soc.*, 1980, **102**, 6344-6346.
76. S. Kraft, E. Hanuschek, R. Beckhaus, D. Haase and W. Saak, *Chem. Eur. J.*, 2005, **11**, 969-978.
77. I. M. Piglosiewicz, R. Beckhaus, W. Saak and D. Haase, *J. Am. Chem. Soc.*, 2005, **127**, 14190-14191.
78. S. Kraft, R. Beckhaus, D. Haase and W. Saak, *Angew. Chem. Int. Ed.*, 2004, **43**, 1583-1587.
79. M. Horác□ek, P. Štěpnic□ka, J. Kubišta, R. Gyepes and K. Mach, *Organometallics*, 2004, **23**, 3388-3397.
80. V. Kupfer, U. Thewalt, I. Tišlerová, P. Štěpnička, R. Gyepes, J. Kubišta, M. Horáček and K. Mach, *J. Organomet. Chem.*, 2001, **620**, 39-50.
81. J. Hiller, U. Thewalt, M. Polášek, L. Petrusová, V. Varga, P. Sedmera and K. Mach, *Organometallics*, 1996, **15**, 3752-3759.
82. A. Noor, E. Sobgwi Tamne, S. Qayyum, T. Bauer and R. Kempe, *Chem. Eur. J.*, 2011, **17**, 6900-6903.
83. G. La Macchia, F. Aquilante, V. Veryazov, B. r. O. Roos and L. Gagliardi, *Inorg.chem.*, 2008, **47**, 11455-11457.
84. J. Shen, G. P. A. Yap, J.-P. Werner and K. H. Theopold, *Chem. Commun.*, 2011, **47**, 12191-12193.
85. G. Dominguez and J. Perez-Castells, *Chem. Soc. Rev.*, 2011, **40**, 3430-3444.
86. D. Leboeuf, V. Gandon and M. Malacria in *Handbook of Cyclization Reactions*, Vol. 1 (Ed.: S. Ma), Wiley-VCH, Weinheim, 2009, pp. 367-405.
87. P. R. Chopade and J. Louie, *Advanced Synthesis & Catalysis*, 2006, **348**, 2307-2327.
88. S. Kotha, E. Brahmachary and K. Lahiri, *Eur. J. Org. Chem.*, 2005, 4741-4767.
89. J. A. Varela and C. Saá, *Chem. Rev.*, 2003, **103**, 3787-3802.
90. 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**, 10342-10346.
91. A. E. Pohland and W. R. Benson, *Chem. Rev.*, 1966, **66**, 161-197.
92. L. J. Gooßen, N. Rodríguez and K. Gooßen, *Angew. Chem. Int. Ed.*, 2009, **48**, 9592-9594.
93. H.-G. Chen, H.-W. Hsueh, T.-S. Kuo and Y.-C. Tsai, *Angew. Chem. Int. Ed.*, 2013, **52**, 10256-10260.
94. Y. Xie, H. F. Schaefer and R. B. King, *J. Am. Chem. Soc.*, 2005, **127**, 2818-2819.
95. 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**, 4391-4393.
96. G. Merino, K. J. Donald, J. S. D'Acchioli and R. Hoffmann, *J. Am. Chem. Soc.*, 2007, **129**, 15295-15302.
97. B. Xu, Q.-S. Li, Y. Xie, R. B. King and H. F. Schaefer, *J. Phys. Chem. A*, 2009, **113**, 12470-12477.
98. B. Xu, Q.-S. Li, Y. Xie, R. B. King and H. F. Schaefer, *J. Chem. Theory Comput.*, 2010, **6**, 735-746.
99. L. Tang, Q. Luo, Q.-S. Li, Y. Xie, R. B. King and H. F. Schaefer, *J. Chem. Theory Comput.*, 2012, **8**, 862-874.
100. L. Gagliardi and B. O. Roos, *Nature*, 2005, **433**, 848-851.
101. B. O. Roos, P.-Å. Malmqvist and L. Gagliardi, *J. Am. Chem. Soc.*, 2006, **128**, 17000-17006.
102. H. Braunschweig, R. D. Dewhurst, K. Hammond, J. Mies, K. Radacki and A. Vargas, *Science* 2012, **336**, 1420.

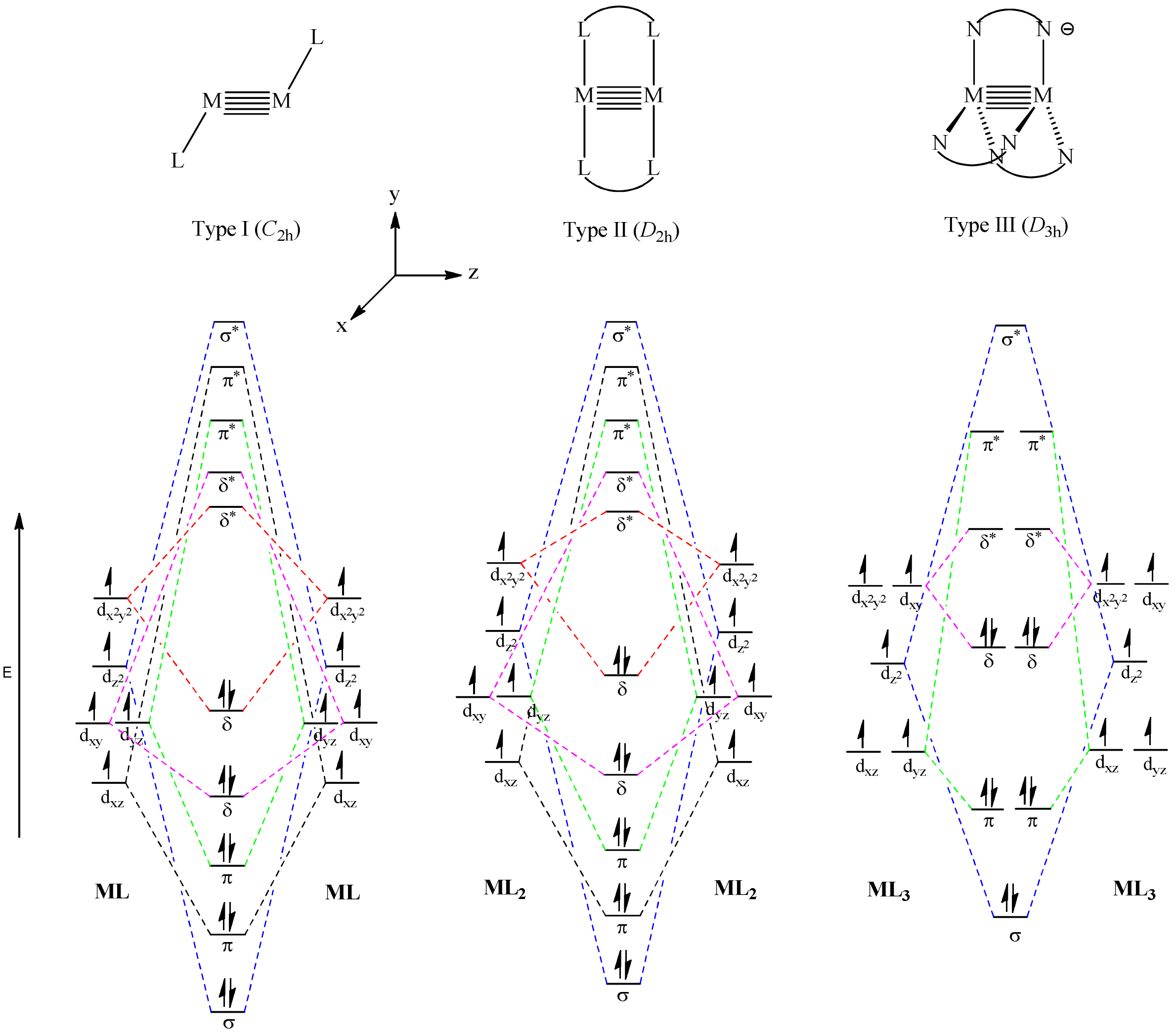


Figure 1. Possible geometries of the quintuple bonded dinuclear complexes and their corresponding qualitative MO diagrams. The type III example is based on compound **11**, where two univalent Cr centres are ligated by three anionic amidinates.

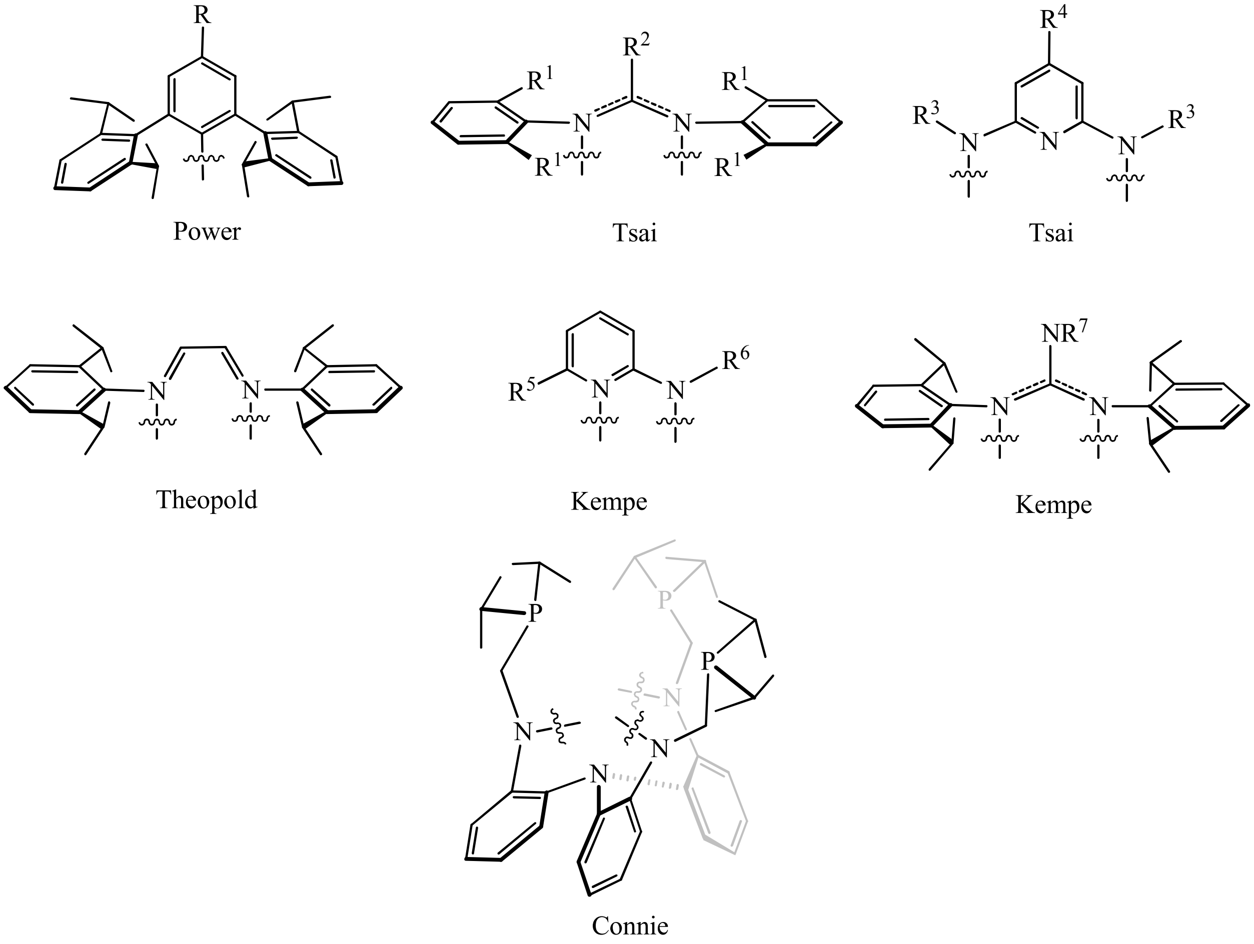
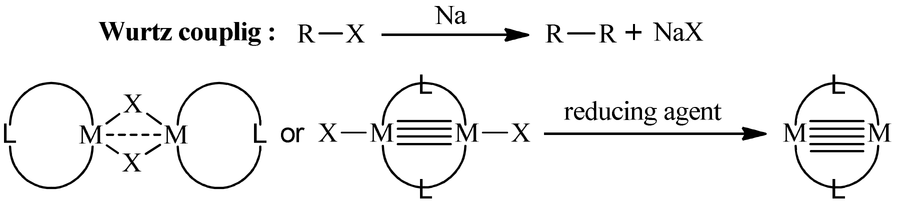
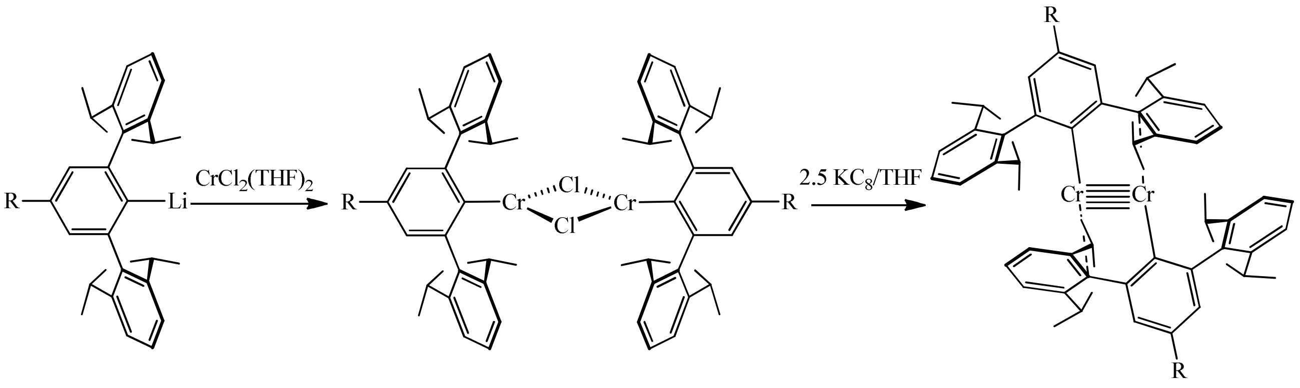


Figure 2. Supporting ligands used to stabilize the metal-metal quintuple bonds.

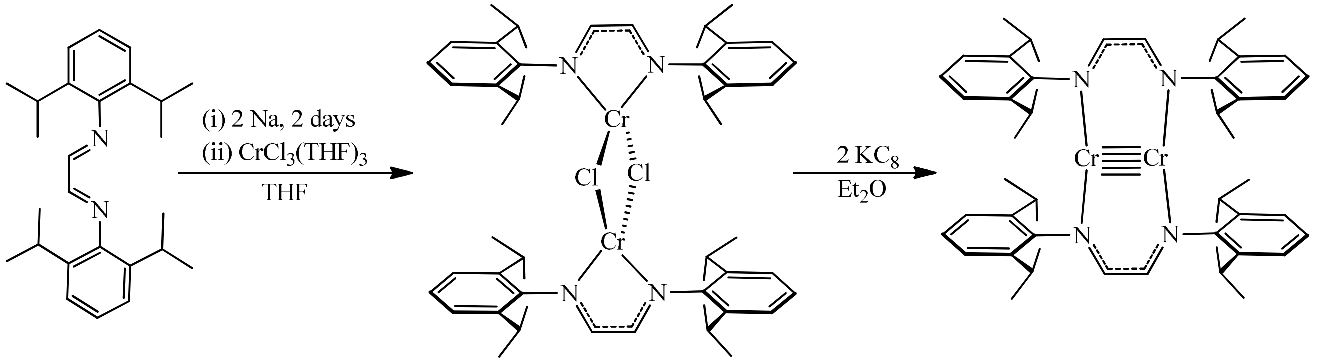


Scheme 1. Parallels between the Wurtz coupling reaction and synthetic pathways of the quintuply bonded dinuclear complexes.



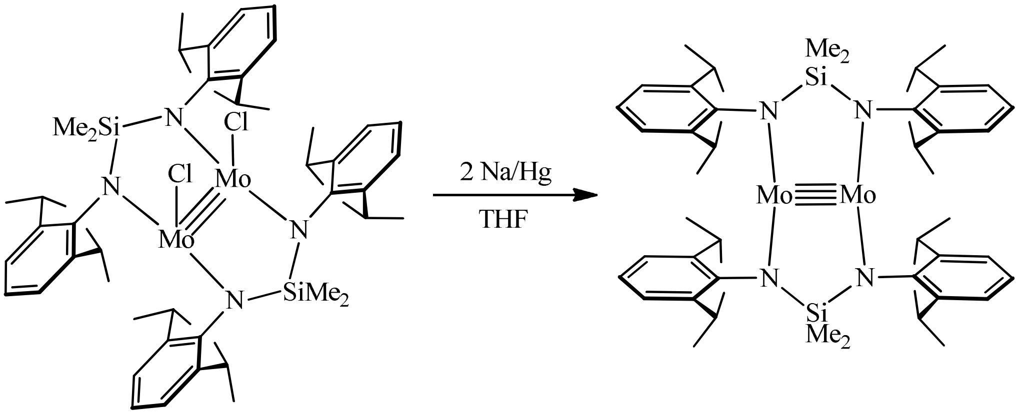
R= H (**1**), $SiMe_3$ (**2**), OMe (**3**), F (**4**)

Scheme 2. Synthetic route for the preparation of the quintuple bonded chromium phenyl dimers **1**-**4**.



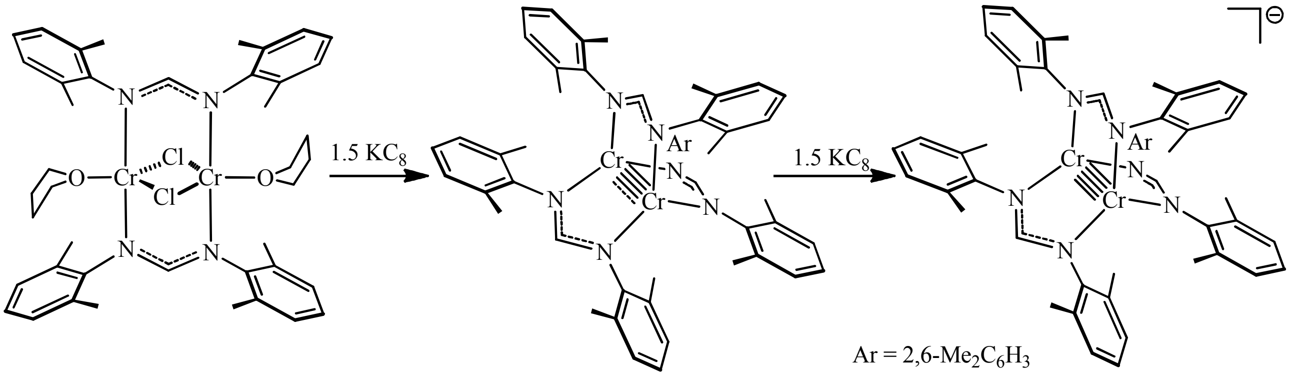
5 **6**

Scheme 3. Synthesis of the quintuple bonded chromium diazadienide dimer **6**.



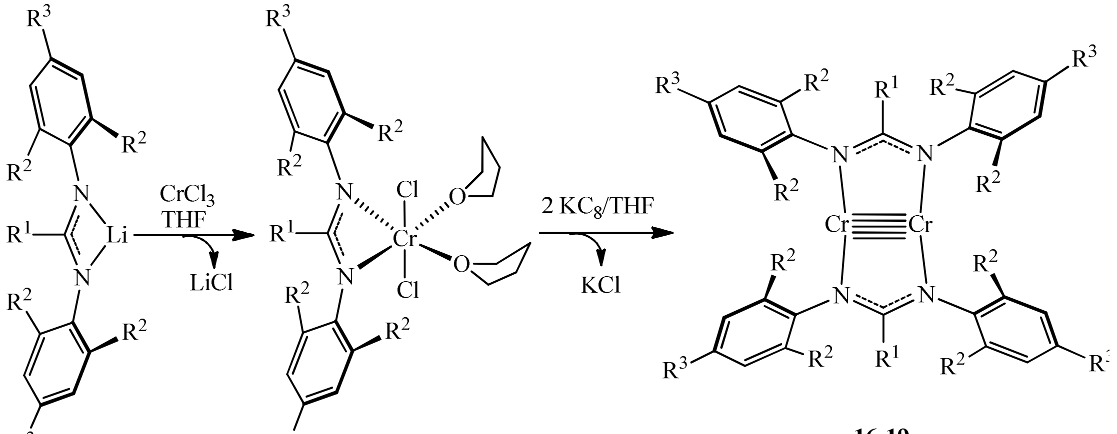
7 **8**

Scheme 4. Synthesis of the quadruple bonded dimolybdenum complex **8**.



9 **10** **11**

Scheme 5. Synthesis of the lantern quintuple bonded dichromium tris(amidinate) complex **11**.



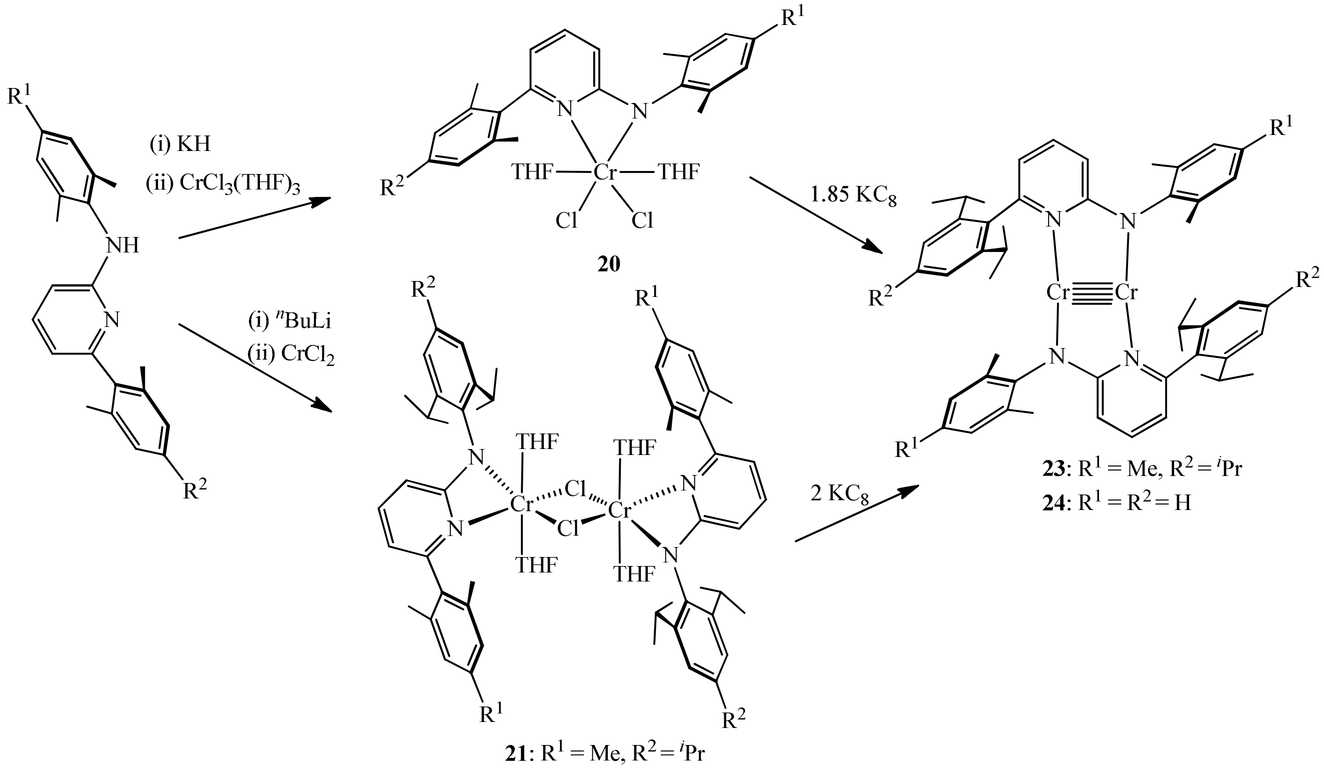
12-15

16-19

12: $R^1 = H, R^2 = R^3 = Me$
13: $R^1 = H, R^2 = Et, R^3 = H$
14: $R^1 = H, R^2 = {}^iPr, R^3 = H$
15: $R^1 = Me, R^2 = {}^iPr, R^3 = H$

16: $R^1 = H, R^2 = R^3 = Me$
17: $R^1 = H, R^2 = Et, R^3 = H$
18: $R^1 = H, R^2 = {}^iPr, R^3 = H$
19: $R^1 = Me, R^2 = {}^iPr, R^3 = H$

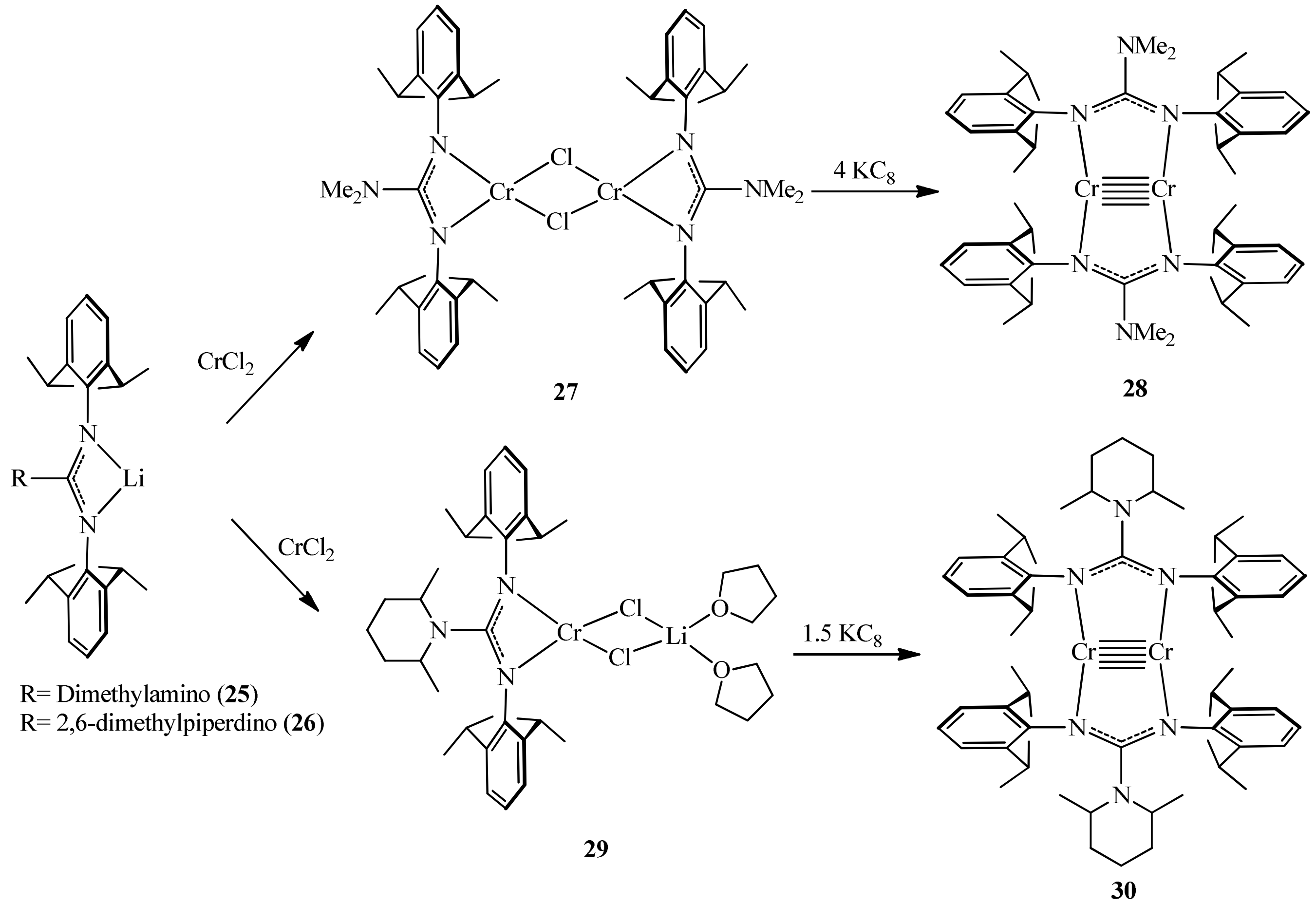
Scheme 6. Synthesis of the quintuple bonded chromium amidinate dimers **16-19**.



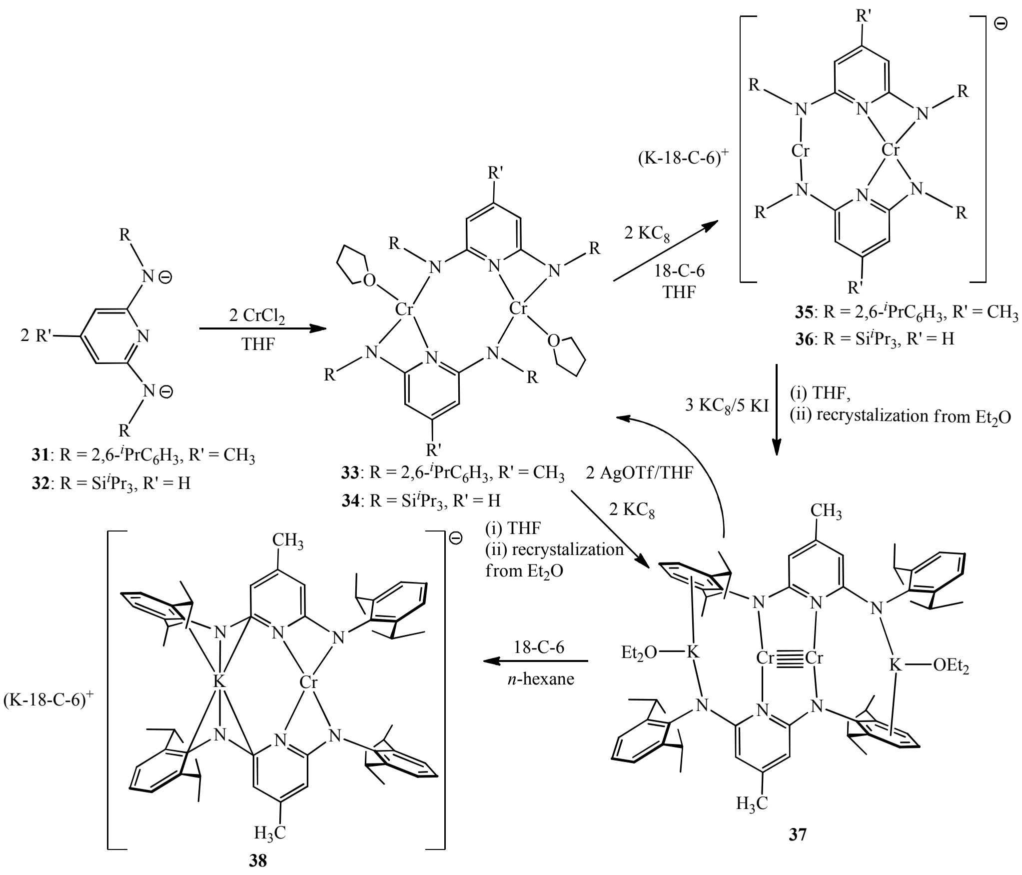
21: R^1 = Me, R^2 = ^{i}Pr
22: R^1 = R^2 = H

23: R^1 = Me, R^2 = ^{i}Pr
24: R^1 = R^2 = H

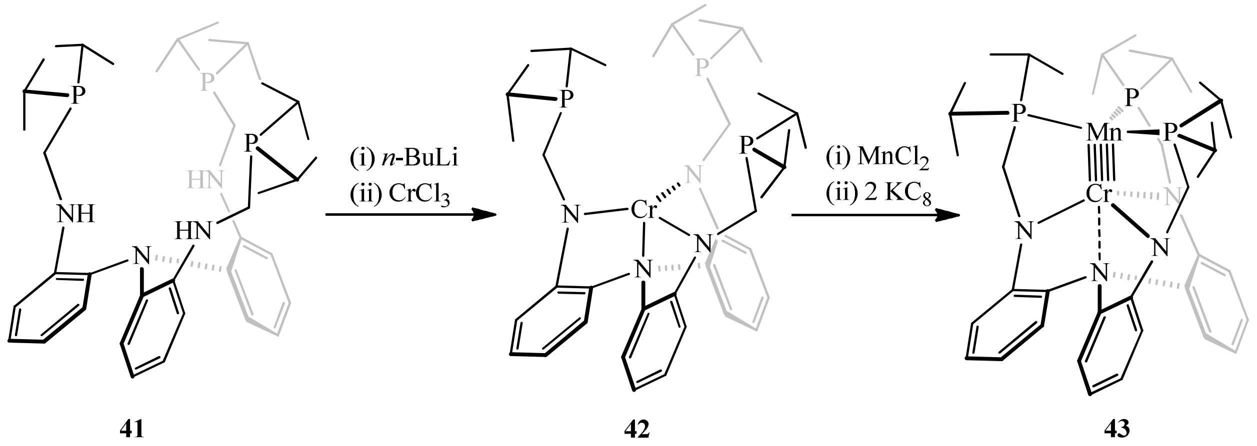
Scheme 7. Synthetic routes of the quintuple bonded chromium pyridylamide dimers **23** and **24**.



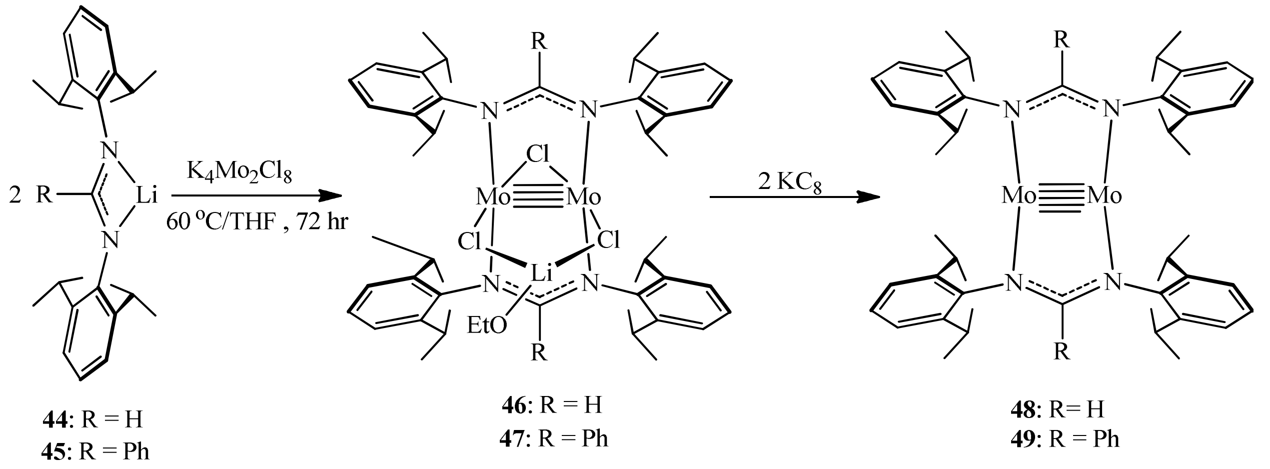
Scheme 8: Synthetic routes of the quintuple bonded chromium guanidinate dimers **28** and **30**.



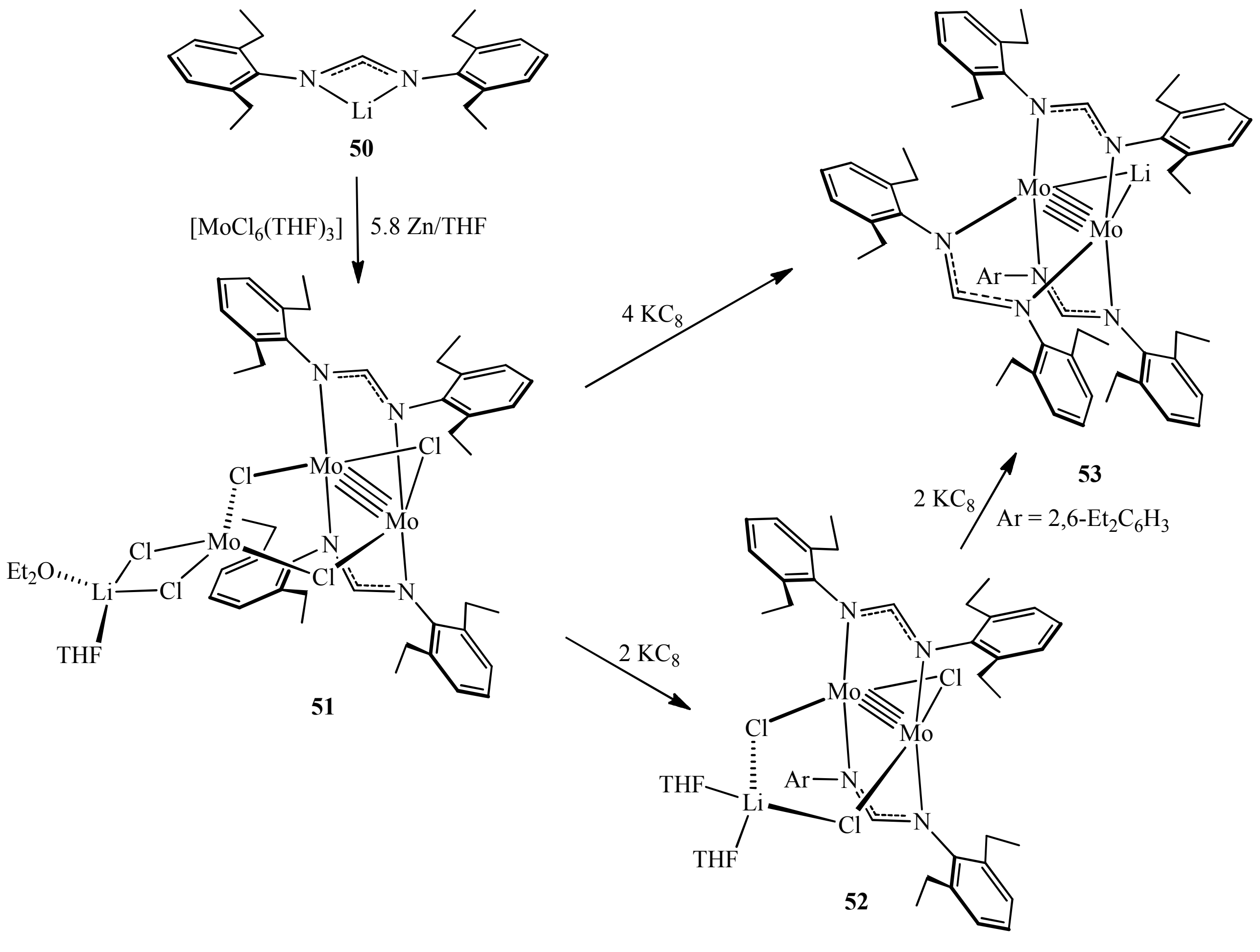
Scheme 9. Synthetic routes for the quintuple bonded chromium pyridyldiamide dimer **37**.



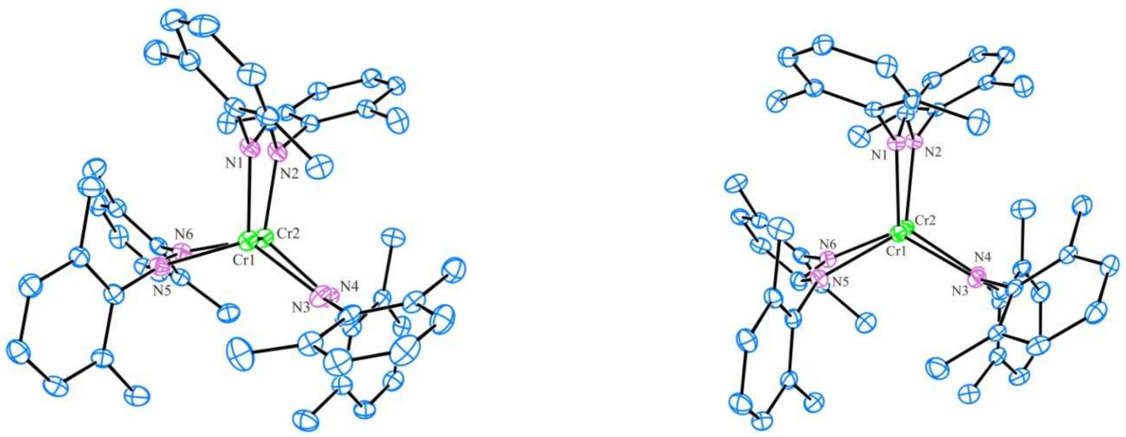
Scheme 10: Synthesis of the heterodinuclear quintuply bonded Cr–Mn complex **43**.



Scheme 11. Synthesis of the quintuple bonded molybdenum amidinate dimers **48** and **49**.

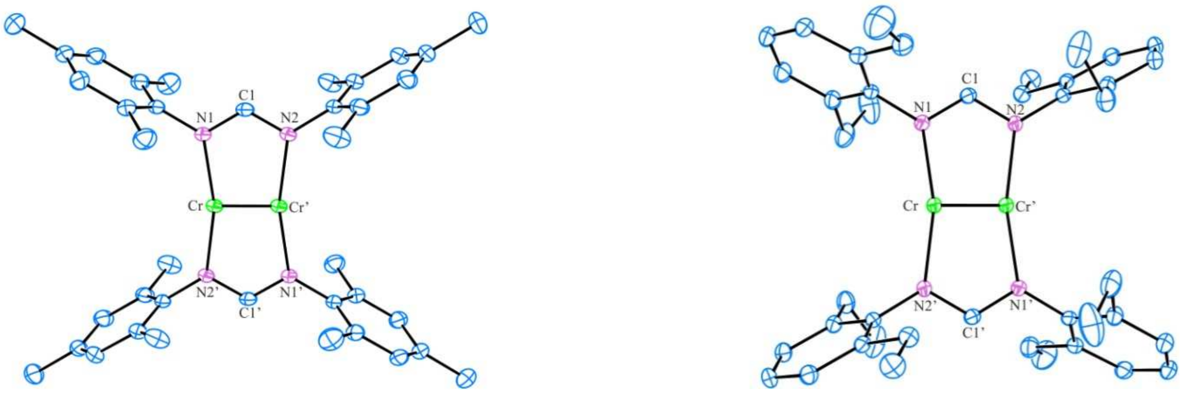


Scheme 12. Synthesis of the lantern quintuple bonded dimolybdenum tris(amidinate) complex **53**.

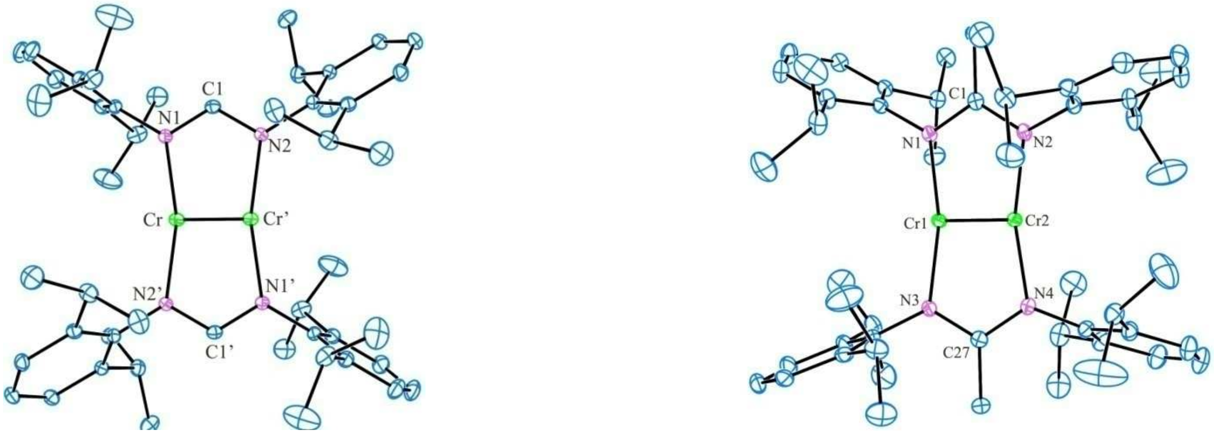


10 (Cr–Cr = 1.8169(7) Å) **11** (Cr–Cr = 1.7397(9) Å)

Figure 3. The solid-state molecular structures of [$Cr_2\{HC(N\text{-}2,6\text{-}Me_2C_6H_3)_2\}_3$] (**10**) and its one-electron reduction anion **11**.

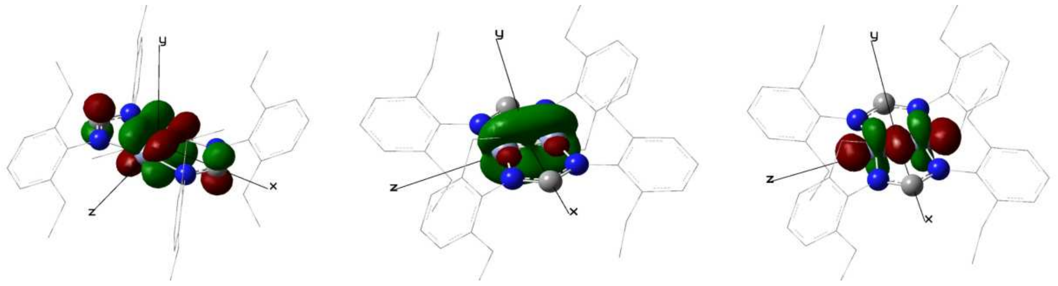


16 (Cr–Cr = 1.7404(8) Å) **17** (Cr–Cr = 1.7454(1) Å)

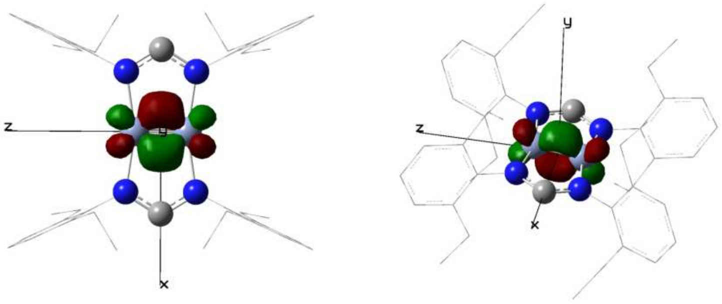


18 (Cr–Cr = 1.7472(10) Å) **19** (Cr–Cr = 1.7395(7) Å)

Figure 4. X-ray crystal structures of the quintuple bonded dichromium amidinates **16-19**.

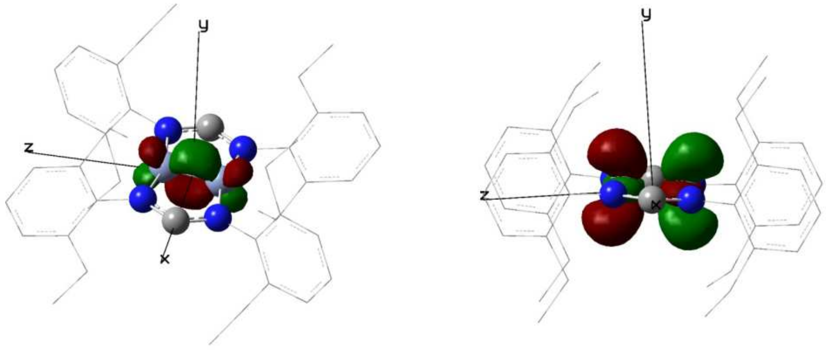


HOMO (–3.814 eV) HOMO−1 (–3.980 eV) HOMO−2 (–5.073 eV)



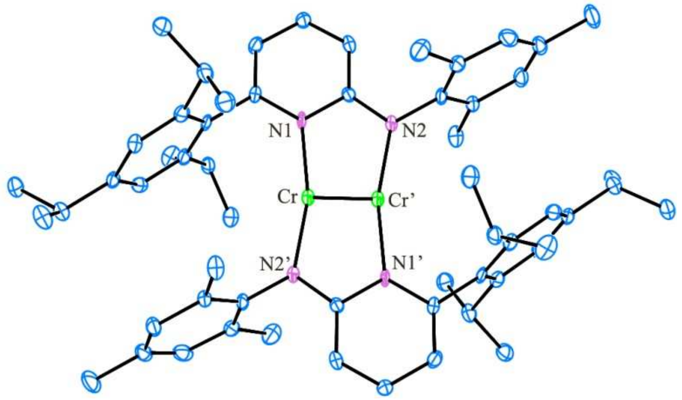
HOMO−3 (–5.507 eV) HOMO−7 (–5.695 eV)

Figure 5. Representation of the Cr–Cr quintuple bonding orbitals of **17**.



LUMO+1 (–1.641 eV) LUMO (–2.118 eV)

Figure 6. Representation of two lowest unoccupied molecular orbitals of **17**.



23 (Cr–Cr = 1.749(2) Å)

Figure 7. X-ray crystal structure of **23**.

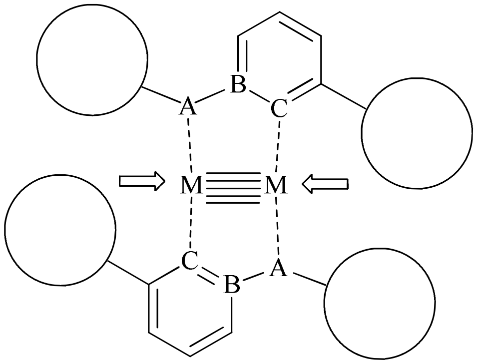
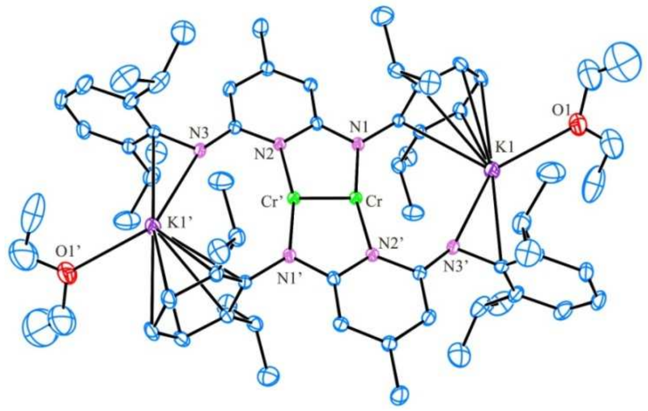
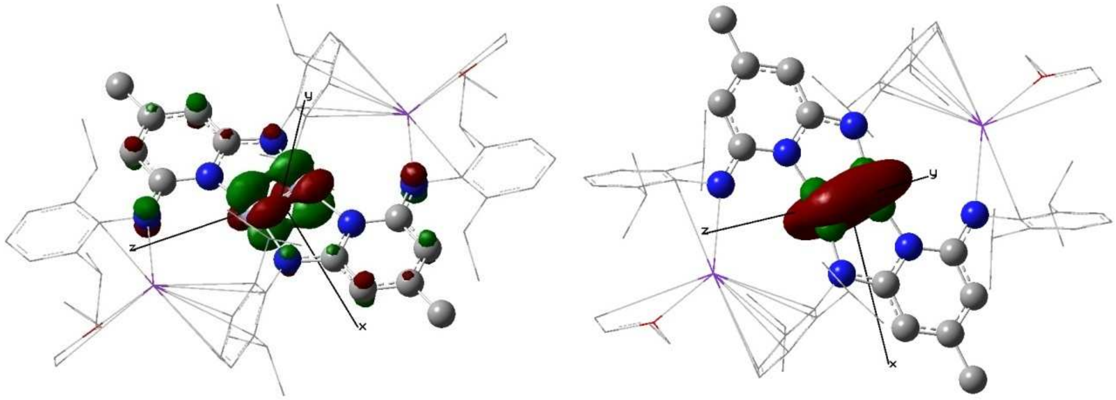


Figure 8. Pictorial representation of how the metal-to-metal bond length affected by metal-ligand interactions.



37 (Cr–Cr = 1.7443(10) Å)

Figure 9. X-ray crystal structure of **37**.

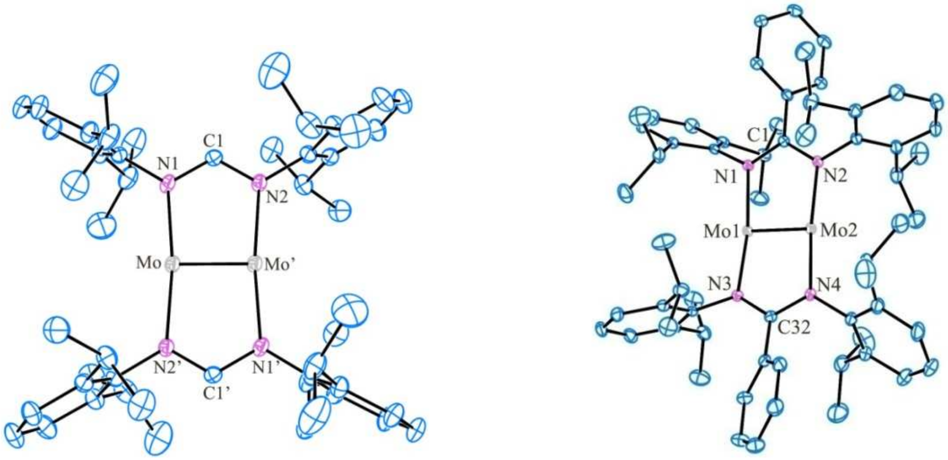


HOMO (–2.456 eV) HOMO−1 (–3.032 eV)

Figure **10**. Representation of HOMO and HOMO–1 of **37**.

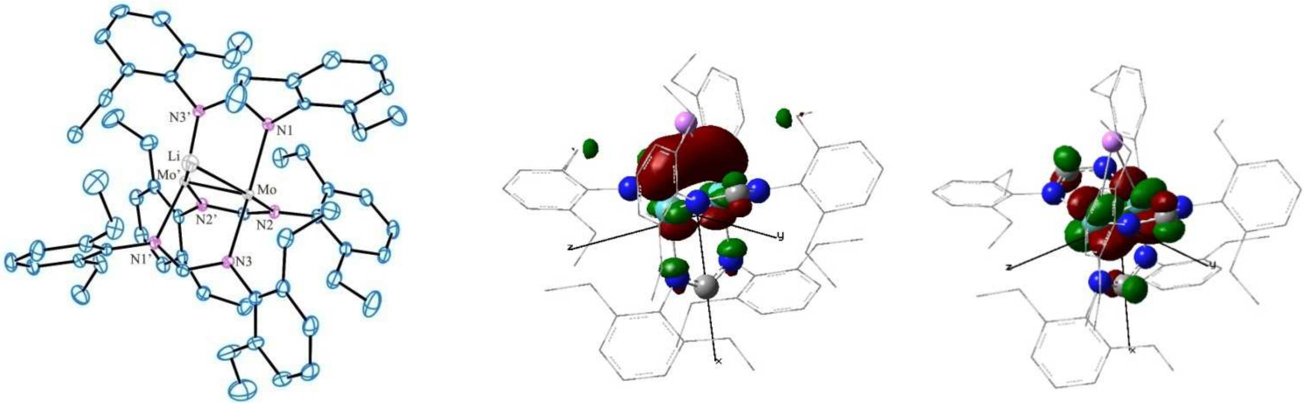
groups	**compounds**	**M-M (Å)**	**formal bond order (FBO)**
Power	**1**	1.8351(4)	5
	2	1.8077(7)	
	3	1.8160(5)	
	4	1.831(2)	
Theopold	**6**	1.8028(9)	
Tsai	**10**	1.8169(7)	
	11	1.7397(9)	4.5
	16	1.7404(8)	5
	17	1.7454(1)	
	18	1.74729(10)	
	19	1.7395(7)	
	48	2.0187(9)	
	49	2.0157(4)	
	37	1.7443(10)	
	53	2.0612(4)	
Kempe	**23**	1.749(2)	
	24	1.750(1)	
	28	1.7293(12)	
	30	1.7056 (12)	
Lu	**43**	1.8192(9)	

Table 1: The structurally characterized quintuple bonded compounds and their metal-metal bond lengths.



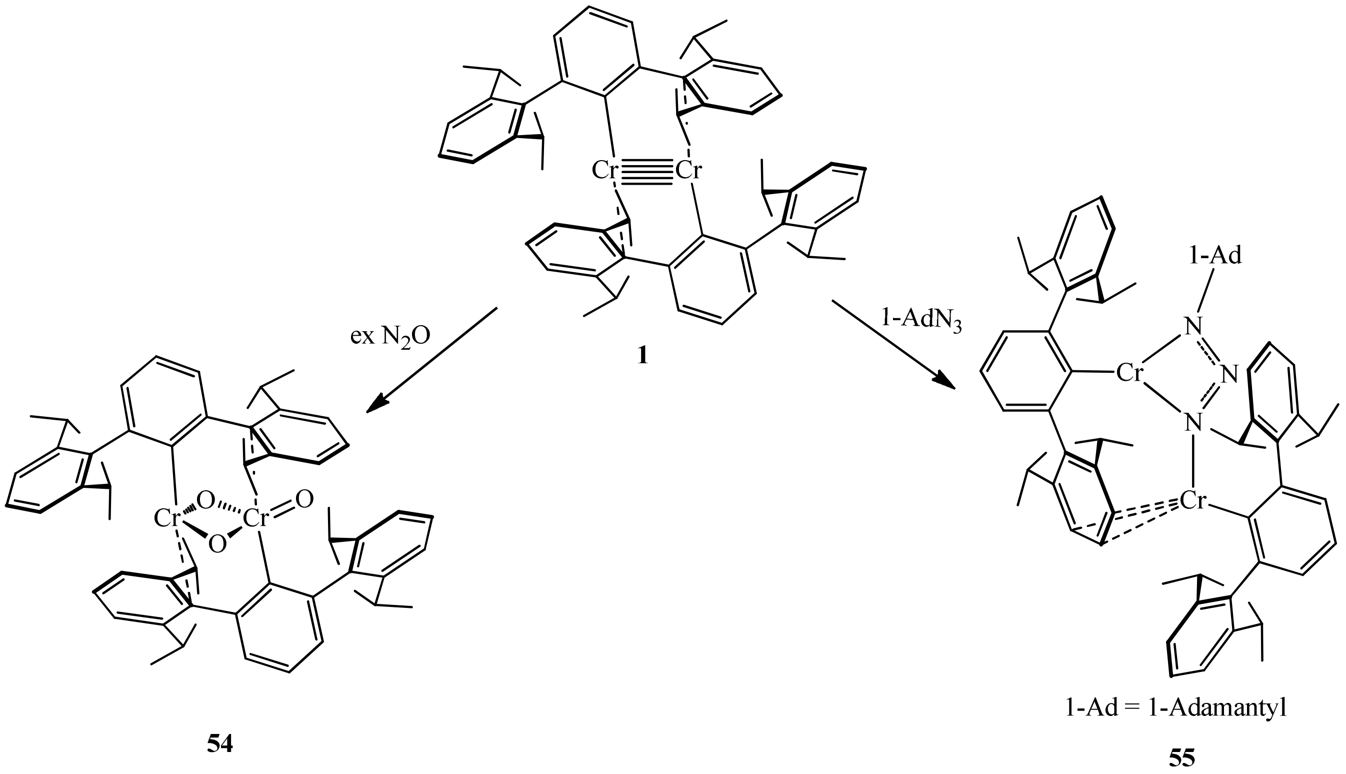
48 (Mo–Mo = 2.0187(9) Å) **49** (Mo–Mo = 2.0157(4) Å)

Figure 11. X-ray crystal structures of **48** and **49**.

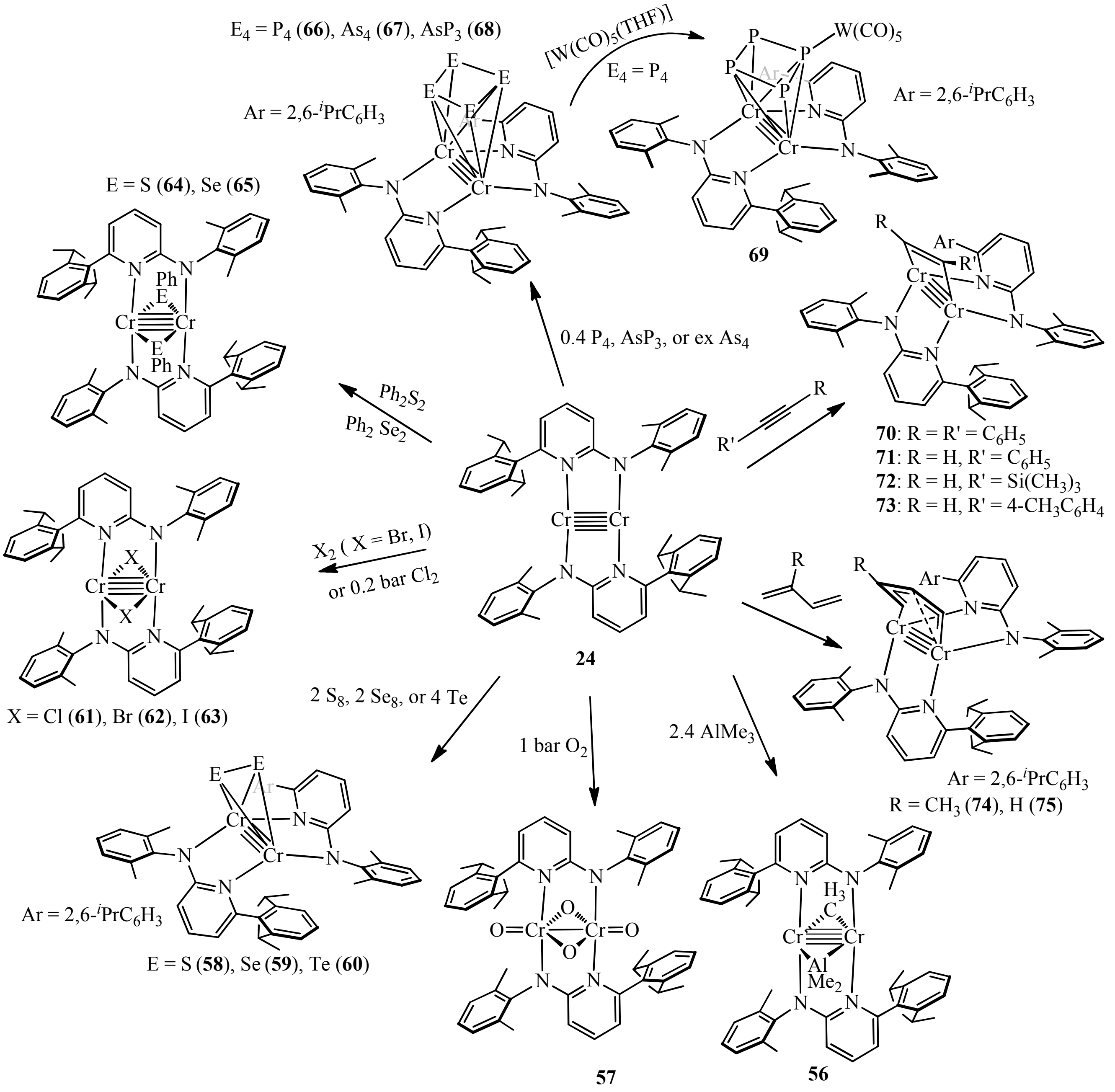


53 (Mo–Mo = 2.0612(4) Å) HOMO HOMO−1

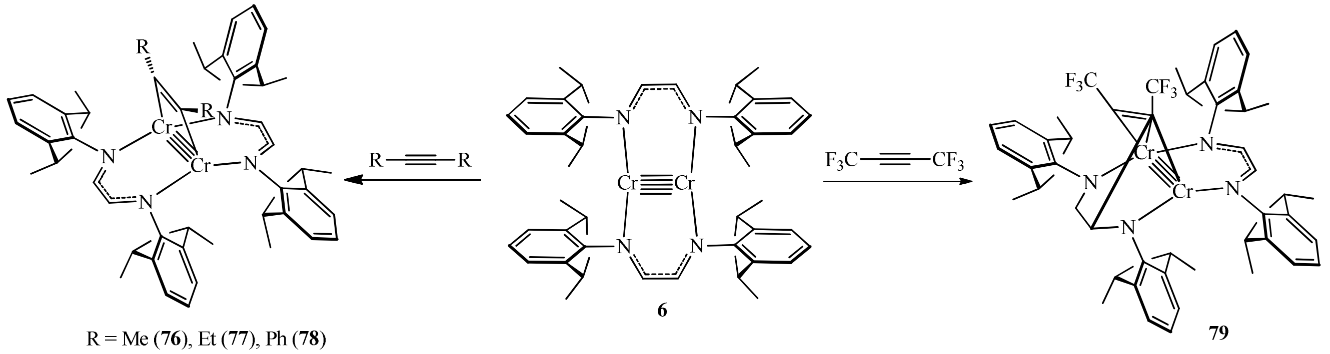
Figure 12. X-ray crystal structure of **53** and representation of its HOMO and HOMO−1.



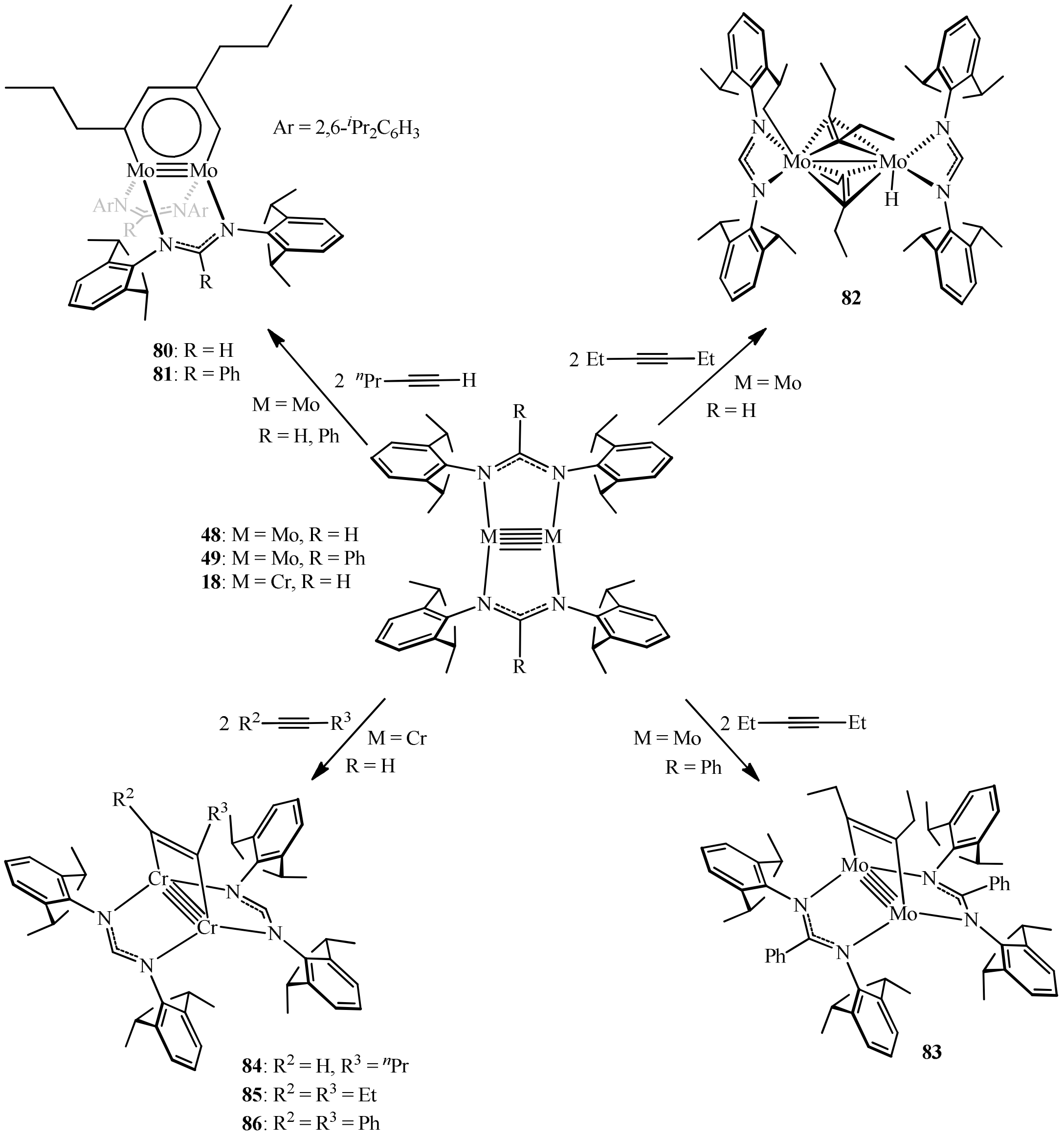
Scheme 13. Reactions of **1** with nitrous oxide and 1-adamantyl azide.



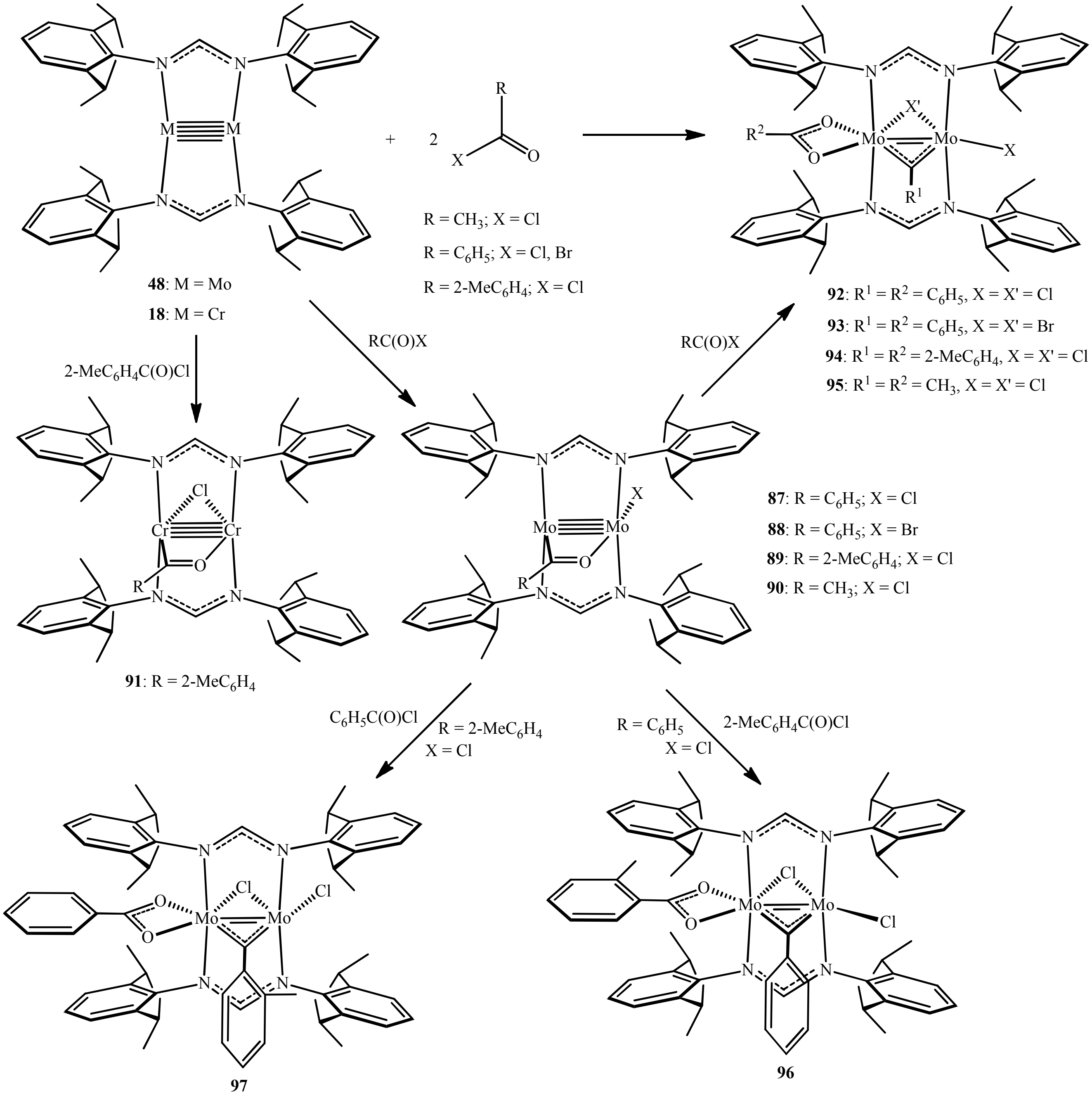
Scheme 14. Reaction pinwheel highlighting the chemistry of **24**.



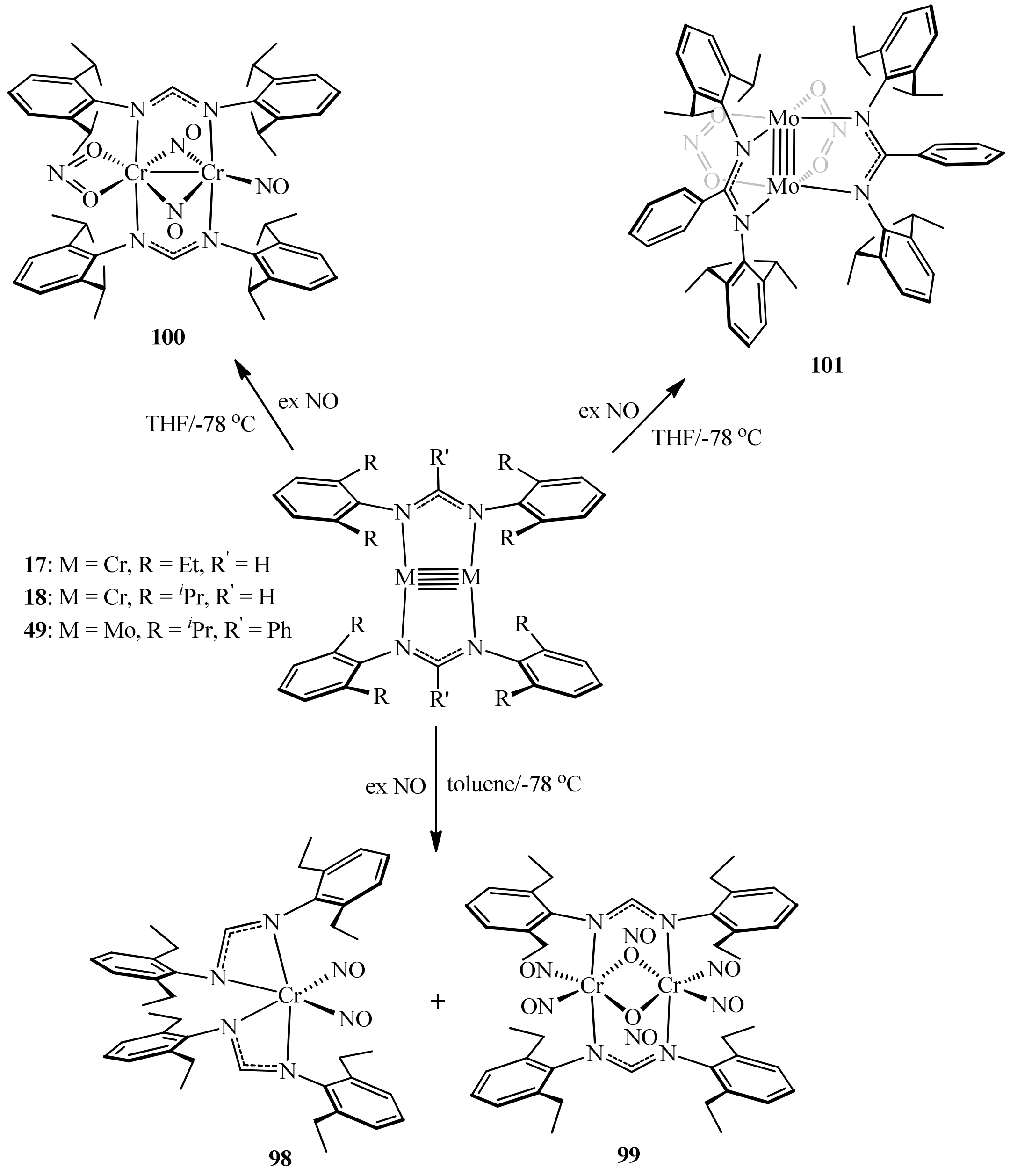
Scheme 15. [2+2] reaction of **6** with internal alkynes.



Scheme 16. Cycloaddition of the quintuple bonded chromium and molybdenum amidinate dimers with alkynes.



Scheme 17. Reactions of the quintuple bonded chromium and molybdenum amidinate dimers with acyl halides.



17: M = Cr, R = Et, R' = H
18: M = Cr, R = ^{i}Pr, R' = H
49: M = Mo, R = ^{i}Pr, R' = Ph

Scheme 18. Divergent reactivity of nitric oxide with the quintuple bonded group VI amidinate dimers **17**, **18** and **49**.