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Pushing the limits of electron donation for *cis*-chelating ligands *via* an alliance of phosphonium ylide and anionic abnormal NHC†

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The grafting of a $-(CH_2)_2PR_3^+$ moiety on an NHC ligand backbone in the Mn(I) complex [Cp(CO)$_2$Mn(IMes)] followed by double deprotonation opens a route to bidentate ligands with extreme electron-donating character. Such remarkable electronic properties can even allow intramolecular sp^2 C–H functionalization in typically inert square-planar Rh(I) dicarbonyl complexes.

Strongly electron-donating ligands have been widely investigated over the last three decades, leading to decisive advances in many fields such as homogeneous catalysis,[1] photophysics[2] and materials science.[3] The isolation of the first stable 2*H*-imidazol-2-ylidene (**A**, Chart 1) by Arduengo in 1991[4] was a key milestone in this continuing quest, from which N-heterocyclic carbenes (NHCs) became essential for modern chemistry. The successive preparations of imidazol-4-ylidene (**B**)[5] and anionic imidazol-2,4-diylidene (**C**),[6] so-called "abnormal" (*a*NHC)[7] and "ditopic" (*d*NHC)[8] carbenes, were integral parts of the progress made to access increasingly electron-donating carbon ligands based on the imidazolyl core (Chart 1, top).[9] Indeed, aNHC ligands **B** exhibit stronger σ-donor and weaker π-acceptor character than their "normal" NHC counterparts **A**[10] and these electronic effects are even more pronounced in *d*NHCs metallated at the C2 position,[11] due to the presence of an additional delocalized negative charge in the heterocyclic moiety. Beyond different classes of NHCs, phosphonium ylides derived from triarylphosphines (**D**) and trialkylphosphines (**E**) (Chart 1, down) constitute an alternative class of electron-rich neutral *C*-ligands for transition metals[12] and main group elements.[13] Moreover, a systematic IR spectroscopy investigation of a series of *C*,*C*-chelating Rh(I) dicarbonyl complexes with three different combinations of NHC (**A**) and phosphonium ylide (**D**) donor extremities revealed a decrease in the average ν_{CO} stretching frequencies in the order **A–A** > **A–D** > **D–D**, thus demonstrating the superior electron donation of phosphonium ylide *vs.* conventional NHC (Chart 1, bottom).[14] In addition, it was recently shown for Pd(II) carbonyl complexes that a PCy$_3$-derived phosphonium ylide fragment (**E**) is an even stronger donor than is its PPh$_3$-containing analogue (**D**).[15] In a logical continuation of our research program focused on the association of classical NHCs with phosphonium ylides in bidentate,[14–16] pincer[15,17] and tetradentate[18] scaffolds, we envisioned to combine for the first time the strongest donors of each family with the aim of approaching the upper limits of the electronic scale in chelating systems.[19] In this contribution, we report the preparation, coordination chemistry with rhodium and evaluation of electronic properties of anionic abnormal NHC/phosphonium ylide ligands

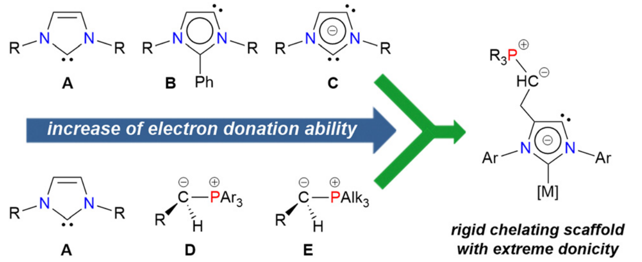

Chart 1 General trends in electron donation for different types of imidazole-based N-heterocyclic carbenes (top) and phosphonium ylides (bottom) as well as the structure of hybrid bidentate ligands proposed in this work (right).

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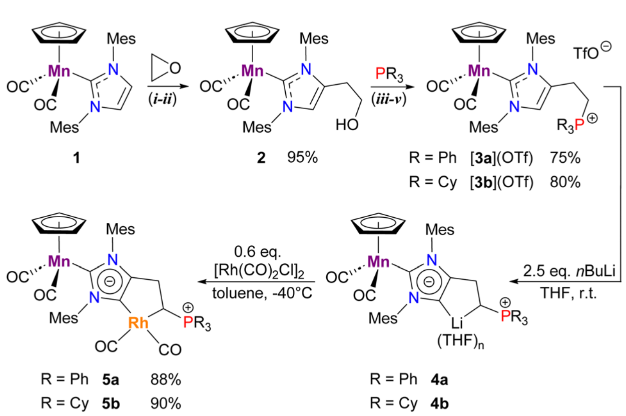
(Chart 1, right) as well as unusual C–H functionalization in Rh(I) dicarbonyl species.

For the assembly of the anionic abnormal carbene platform, we chose a readily available, on a multi-gram scale, Mn(I) complex **1**[20] (Scheme 1) bearing the common 1,3-bis(2,4,6-trimethylphenyl)-2*H*-imidazol-2-ylidene (IMes) ligand, in which the organometallic fragment in addition to protecting the C2 carbene position can also serve as an excellent IR[11] and electrochemical[21] probe. The $-CH_2CH_2OH$ arm required for grafting the phosphonium moiety was installed on the IMes ligand backbone *via* a direct functionalization approach[22] consisting of the deprotonation of **1** with *n*BuLi and the trapping of the resulting anionic abnormal carbene [Cp(CO)$_2$Mn(*d*IMesLi)] with ethylene oxide. The subsequent transformation of complex **2** to the corresponding triflate derivative followed by one-pot quaternization with PPh$_3$ and PCy$_3$ afforded phosphonium pre-ligands [**3a**](OTf) and [**3b**](OTf) in good yields (Scheme 1). Both of them were fully characterized and their exact structures were obtained using X-ray diffraction (Fig. 1). Their deprotonation with 2.5 eq. of *n*BuLi in THF at room temperature led to a nearly quantitative generation of extremely moisture-sensitive *a*NHC-ylides **4a** and **4b** as confirmed by IR spectroscopy having revealed the presence of two low-frequency ν_{CO} bands (Table 1) characteristic for Mn(I) complexes bearing anionic *a*NHC ligands.[20,22] The coordination of these species with a slight excess of [Rh(CO)$_2$Cl]$_2$ dimer was performed in toluene at low temperature similarly as described earlier for the related MnFe *d*IMes derivative,[11] leading to the zwitterionic complexes **5a** and **5b** isolated in excellent yields (Scheme 1).

The identity of heterobimetallic MnRh complexes **5a** and **5b** was confirmed from spectroscopic methods and HRMS data. IR spectra of both products showed two pairs of ν_{CO} bands in an approximately 1 : 1 intensity ratio (Fig. S23, S24, ESI† and Table 1) in agreement with a presence of [Mn(CO)$_2$] and [Rh(CO)$_2$] fragments exhibiting a *cis*-arrangement of carbonyl groups. The presence of a P-ylide moiety coordinated to the Rh(I) center was confirmed by the observation of ^{31}P NMR signals at δ_P 41.2 and 43.6 ppm for **5a** and **5b**, respectively, being deshielded compared to those of their phosphonium precursors ([**3a**](OTf): δ_P 22.7 ppm; [**3b**](OTf): δ_P 31.3 ppm) as well as characteristic high-field ^{13}C resonances with appropriate multiplicity (**5a:** δ_C 13.9 ppm (dd, $^1J_{CRh}$ = 27.5 Hz, $^1J_{CP}$ = 25.5 Hz); **5b:** δ_C 6.4 ppm (dd, $^1J_{CRh}$ = 25.7 Hz, $^1J_{CP}$ = 19.6 Hz)). The characteristic **5a** and **5b** ^{13}C NMR signals resulting from the carbenic atoms of anionic imidazol-2,4-diylidenes were observed as singlets at δ_C 199.9–200.5 ppm (C2) and doublets at δ_C 162.2–162.7 ppm with a $^1J_{CRh}$ coupling constant of *ca.* 42 Hz (C4). Finally, each of the bimetallic complexes yielded four distinct ^{13}C NMR spectral CO signals and a full set of inequivalent resonances of mesityl groups, probably due to blocked rotation across their respective C–N bonds and the existence of a chiral center in the NHC backbone.



Scheme 1 Synthesis of anionic *a*NHC-phosphonium ylide ligands **4a–b** and their Rh(I) complexes **5a–b**. Reaction conditions: (i) 1.2 eq. *n*BuLi, THF, r.t., 2 h; (ii) 2 eq. ethylene oxide, −40 °C to r.t., 2 h; (iii) 1.1 eq. *n*BuLi, THF, r.t., 20 min; (iv) 1.1 eq. Tf$_2$O, PhCl, −40 °C to r.t., 1 h; (v) 3.0 eq. PPh$_3$ or 1.5 eq. PCy$_3$, PhCl, 60–80 °C, 16 h.

Inspection of the X-ray diffraction structure acquired of complex **5a** (Fig. 1) showed the Rh(I) atom in a square-planar environment with the *d*IMes-ylide behaving as a *cis*-chelating ligand. While the Rh–carbene bond distance (2.045(2) Å) was measured to be very close to the values found in other Rh(I) complexes bearing IMes-derived *a*NHCs (2.038(3)–2.061(4) Å),[23] the Rh-ylide bond (2.189(2) Å) was found to be slightly longer than those of similar bidentate ylide structures (2.1250(14)–2.155(8)).[14,24] The Rh–CO bond in the position *trans* to the *a*NHC moiety was also observed to be slightly longer than that opposite to the phosphonium ylide, presumably reflecting higher *trans* effect of the former ligand. Inspection of the structure also showed, notably, the 5-membered rhodacycle to be virtually coplanar with the NHC fragment. And structural comparisons showed the NHC–Rh-ylide angle in **5a** (78.98(8)°) to be significantly more acute that those observed in Rh(I) (94.0(3)°)[14] or Pd(II) (91.9(2)°)[16a] NHC-ylide complexes featuring more flexible 7- and 6-membered chelating cycles, respectively, and to be comparable only with those of related species based on more rigid NHC-bis(ylide) ligands (82.61(6)–85.85(5)°)[25] with a similar size of the metallacycle.

Access to the Rh(I) dicarbonyl derivatives **5a–b** provided a perfect opportunity to quantify the electronic properties of the novel *a*NHC-ylide ligands using the frequencies of ν_{CO} bands in solution IR spectra, which is applicable for benchmarking both mono-[9] and bidentate ligands.[19] While ν_{CO} values for the [Cp(CO)$_2$Mn] fragment in **5a** and **5b** were observed to be almost the same (Table 1) and to remain very close to that of the previously reported *d*IMes complex,[11] the average $\langle\nu_{CO}\rangle$ value for the [Rh(CO)$_2$] moiety of **5b** was found to be *ca.* 10 cm^{-1} lower, consistent with the higher electron-donation ability of PCy$_3$-derived ylide *vs.* its PPh$_3$ analogue. The same trends were confirmed using cyclic voltammetry studies revealing a reversible Mn(I)/Mn(II) oxidation wave at −0.38 V *vs.* Fc/Fc$^+$ followed by the occurrence of irreversible one-electron oxidation at +0.61 and +0.51 V *vs.* Fc/Fc$^+$ for the Rh(I) moiety in complexes **5a** and **5b**, respectively. Very importantly, the values of the $\langle\nu_{CO}\rangle$ parameter for both **5a** (2001 cm^{-1}) and **5b** (1991 cm^{-1}) were observed to be far lower than those for known Rh(I) dicarbonyl complexes bearing bis(NHC) (2057 cm^{-1}),[14] phosphine-phosphonium ylide (2053 cm^{-1}),[24a] bis(1,2,3,-triazol-4-ylidene)

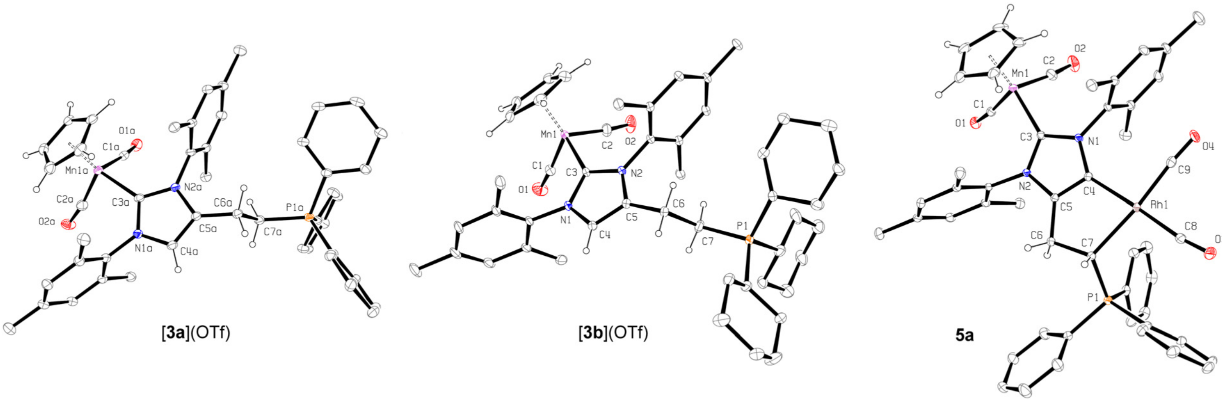


Fig. 1 Molecular geometries of complexes [**3a**](OTf), [**3b**](OTf) and **5a** (25% probability ellipsoids, hydrogen atoms of aryl groups, co-crystallized solvent molecules and counter-anions are omitted for clarity). Selected bond lengths [Å], and angles (°). [**3a**](OTf): Mn1a–C3a 2.012(3), C4a–C5a 1.344(4), C7a–P1a 1.805(3); [**3b**](OTf): Mn1–C3 2.012(2), C4–C5 1.337(3), C7–P1 1.806(3); **5a**: Mn1–C3 2.011(2), C4–C5 1.349(3), Rh1–C4 2.045(2), Rh1–C7 2.189(2), C7–P1 1.769(2) Rh1–C8 1.890(2), Rh1–C9 1.868(2), C4–C5 1.399(3), C4–Rh1–C7 78.98(8), C4–Rh1–C8 176.67(10), C7–Rh1–C9 174.16(8), C8–Rh1–C9 87.43(10), P1–C7–Rh1 115.69(10), C4–C5–C6–C7 3.9(3).

Table 1 Experimental IR data for complexes **4–6** in THF solution and the corresponding ν_{CO} frequency values computed at the wb97xd/tzvp level

	Experimental ν_{CO} (THF, cm^{-1})		Calculated ν_{CO} (non-scaled, cm^{-1})	
No.	$[Mn(CO)_2]$	$[Rh(CO)_2]$	$[Mn(CO)_2]$	$[Rh(CO)_2]$
4a	1899, 1829	—	2028, 1966	—
4b	1898, 1828	—	2028, 1965	—
5a	1906, 1838	2035, 1966	2032, 1969	2147, 2079
5b	1906, 1838	2030, 1952	2031, 1968	2139, 2065
6a	1912, 1845	2034, 1966	2040, 1979	2143, 2078

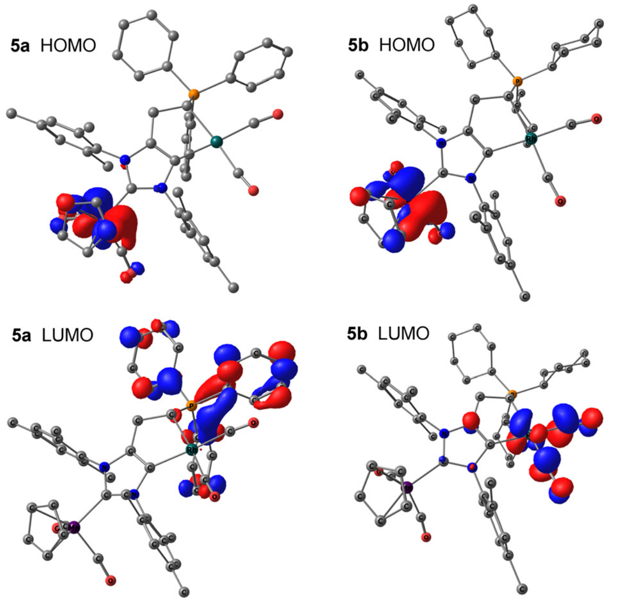
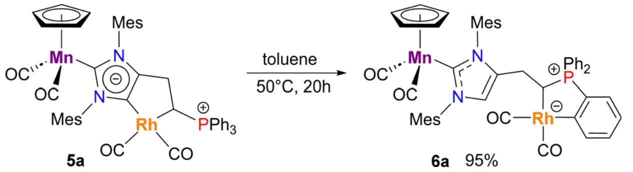


Fig. 2 Frontier molecular orbitals of complexes **5a** and **5b** (isosurface set at 0.05 a.u.).

(2047–2048 cm^{-1}),[26] NHC-iminophosphorane (2046 cm^{-1}),[27] NHC-phosphonium ylide (2039 cm^{-1})[14] and bis(phosphonium ylide) ligands (2017 cm^{-1}),[14] thus highlighting the extreme donation ability of our developed systems.

Intrigued by these outstanding electronic properties, we decided to study the structure and bonding situation in bimetallic species by performing DFT calculations. To our delight, all the trends observed in the experimental IR spectra of **4a–b** and their Rh(I) complexes **5a–b** were essentially perfectly reproduced in the ν_{CO} frequency calculations (Table 1). The calculations yielded rather similar HOMOs localized at the $[CpMn(CO)_2]$ moiety in both species (Fig. 2, top), but markedly different LUMOs for **5a** and **5b**, revealing the main contribution of PPh_3^+ and $[Rh(CO)_2]$ fragments, respectively (Fig. 2, bottom). The global AIM charge of the $[Rh(CO)_2]$ fragment in complex **5b** was found to be slightly lower than that in the case of **5a** (0.171 *vs.* 0.177), consistent with a stronger electron donation of the PCy_3-derived ylide moiety. Interestingly, the AIM charge distribution in carbonyl ligands coordinating the Rh(I) center in bimetallic complexes was found to be quite asymmetrical, accumulating more electron density on the CO in the position *trans* to the *a*NHC ligand (−0.207 and −0.225 for **5a** and **5b**, respectively) than on those having the *cis* arrangement (*ca.* −0.160). An ETS-NOCV analysis of the NHC-ylide bonding (Fig. S4, see the ESI† for details)—beyond showing the major primary channel responsible for σ-donation from both *C*-ligands to the $[Rh(CO)_2]$ unit—also revealed an additional channel for the *a*NHC moiety having *ca.* 40% weaker associated energy, with the charge flowing only to the metal atom and opposite CO ligand (Fig. S4, ESI†). These results seemed to indicate the anionic *a*NHC ligand to be a stronger σ-donor than neutral phosphonium ylide regardless of the occurrence of some π-retrodonation for the metal–carbene bond (Fig. S5, ESI†).

Unlike complex **5b**, which was observed to be stable in solution over long periods of time, its PPh_3^+ analogue **5a** slowly transformed even at room temperature to another species, namely **6a**, isolated in 95% yield after being heated at 50 °C (Scheme 2). While IR and cyclic voltammetry data for $[Rh(CO)_2]$ remained virtually unchanged (Table 1), both ν_{CO} frequencies (1912, 1845 cm^{-1})[11] and oxidation potential (−0.32 V *vs.*



Scheme 2 Transformation of complex **5a** into its isomer **6a** *via* cyclometallation with the phenyl ring of the phosphonium moiety.

Fc/Fc$^+$)[21] of the Mn(I) center clearly indicated its coordination with a regular imidazol-2-ylidene ligand, which was consistent with the re-appearance of the characteristic ^{13}C NMR resonance of the CH moiety belonging to the NHC backbone (δ_C 122.9 ppm). Finally, the presence of the coordinated ylide moiety (δ_C 22.5 ppm, dd, $^1J_{CP}$ = 32.2 Hz, $^1J_{CRh}$ = 24.1 Hz) and downfield signal at δ_C 181.6 (pseudo t, $^1J_{CRh}$ = $^2J_{CP}$ = 33.7 Hz) characteristic for cyclometallated phosphonium fragment,[17] unambiguously confirmed the structure of **6a** as a zwitterionic heterobimetallic MnRh species bearing a bidentate aryl/phosphonium ylide ligand. A preliminary hypothesis concerning the formation of complex **6a** might include the intramolecular activation of the *ortho*-C–H bond of a P$^+$–Ph substituent by the electron-rich metal site followed by a reductive elimination of the *a*NHC ligand in a putative Rh(III) hydride intermediate. Despite an extensive use of Rh(I) derivatives in catalytic C–H functionalization,[28] this transformation represented the first example, to the best of our knowledge, of intramolecular sp^2 C–H functionalization in typically inert square-planar Rh(I) dicarbonyl complexes.[29]

In summary, we have combined, for the first time, anionic abnormal carbene and phosphonium ylide to obtain structurally rigid *cis*-chelating ligands with extreme electron-donating properties. The incorporation of alkyl substituents at the phosphorus atom in such scaffolds improved both ligand donicity and stability of the resulting transition metal complexes. The application of these ligands in homogeneous catalysis as well as the studies on the comparison of electronic donation between *a*NHC and phosphonium ylide is currently ongoing in our group.

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Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

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