Reactivity of electrophilic μ-phosphinidene complexes with N-heterocyclic carbenes: formation of the first main group element adducts of 'abnormal' carbene ligands†

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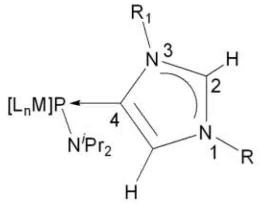
Received (in Berkeley, CA, USA) 21st March 2006, Accepted 25th April 2006
First published as an Advance Article on the web 18th May 2006
DOI: 10.1039/b604150g

The reactions of Mn_2- and Co_2-containing μ-PN^{i}Pr$_2$ complexes with NCN carbenes afford the 'abnormal' carbene adducts [$Mn_2(CO)_8${μ-P(N^{i}Pr$_2$)}(4-cyclo-C_3H_2-1,3-(NR)$_2$))] and [$Co_2(CO)_4$(μ-dppm){μ-P(N^{i}Pr$_2$)(4-cyclo-C_3H_2-1,3-(NR)$_2$)}] (R = ^{t}Bu, adamantyl), respectively.

The isolobal relationship[1] between well known carbene ligands (CR_2) and the less familiar phosphinidene (PR) fragments has prompted vigorous research into the chemistry of transition metal complexes of these latter groups. As has been found with carbene complexes, phosphinidenes can exhibit either nucleophilic (Schrock type)[2] reactivity or electrophilic (Fischer type)[3] characteristics. Recently, we have achieved the isolation of thermally stable, terminal, electrophilic aminophosphinidene (η^1-PNR$_2$) complexes of the mid[4] to late[5] transition metals. These complexes have shown diverse reactivity patterns, ranging from adduct formation with Lewis bases,[3,4c] conversion into η^1-phosphaazines or η^1-phosphaalkenes, and the formation of η^3-diazaphosphaallenes.[6]

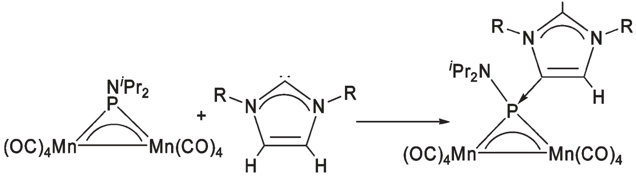
We have also described the synthesis and reactivity of related bimetallic complexes containing trigonal-planar, electrophilic μ-PNR$_2$ ligands and their transformation into σ–π phosphinidene sulfide,[7] σ–π phosphaimine and σ–π phosphaazaimine complexes.[8] Owing to the carbenoid nature of the phosphinidene fragment, we thought that reactions of these complexes with Arduengo carbenes[9] would be of interest. These electron rich carbenes not only serve as extremely versatile carbon-based ligands in catalysis[10] but also as useful reagents for carbon–carbon bond forming reactions.[11] We now wish to report the reactivity of [$Mn_2(CO)_8${μ-P(N^{i}Pr$_2$)}][8] (**1**) and [$Co_2(CO)_4$(μ-dppm){μ-P(N^{i}Pr$_2$)}][8] (**2**) towards the carbon-based nucleophiles 1,3-bis(R)imidazol-2-ylidene (R = ^{t}Bu (**3**) and adamantyl (**4**)), which results in the formation of 'abnormal' N-heterocyclic carbene adducts (*i.e.* C-4 adducts) [$Mn_2(CO)_8${μ-P(N^{i}Pr$_2$)(4-cyclo-C_3H_2-1,3-(NR)$_2$)}] (R = ^{t}Bu (**5**) and adamantyl (**6**)) and [$Co_2(CO)_4$(μ-dppm){μ-P(N^{i}Pr$_2$)(4-cyclo-C_3H_2-1,3-(NR)$_2$)}] (R = ^{t}Bu (**7**) and adamantyl (**8**)), respectively. These products arise in a formal sense from the unprecedented coupling of complexes derived from singlet phosphinidenes with free singlet carbenes.



L$_n$M = metal complex; PN^{i}Pr$_2$ = phosphinidene fragment

A

The addition of NCN carbene **3** to [$Mn_2(CO)_8${μ-P(N^{i}Pr$_2$)}] (**1**) in ether results in the precipitation, over several hours, of the lemon-yellow solid [$Mn_2(CO)_8${μ-P(N^{i}Pr$_2$)(4-cyclo-C_3H_2-1,3-(N^{t}Bu)$_2$)}] (**5**) (Scheme 1). The reaction was followed by ^{31}P NMR spectroscopy and no intermediates were observed. Coordination of the NCN carbene to the phosphinidene phosphorus results in a dramatic upfield shift of the resonance for this group from δ 731 in **1** to δ 234 in **5**. The ^{1}H NMR spectrum of the product shows the expected ^{t}Bu and ^{i}Pr resonances, in addition to singlets for the vinylic hydrogens at δ 8.18 and 8.11. The non-equivalence of the latter two signals suggests that the carbene is not bound through C-2 of the carbene precursor. The ^{13}C NMR spectrum of **5** shows a doublet for the P-bound carbon at δ 147.3 ($^1J_{P\text{–}C}$ = 141 Hz), a doublet for C-3 at δ 129.8 ($^2J_{P\text{–}C}$ = 26.7 Hz) and a singlet for C_1 at δ 132.5. The structure was unequivocally determined *via* X-ray crystallography‡ (Fig. 1), which showed, unexpectedly, that the 'ylidene' moiety of the NCN carbene has migrated from the 2- to the 4-position in the carbene precursor (**A** above). The structure features a NCN carbene-stabilized phosphinidene fragment, asymmetrically bridging two approximately eclipsed Mn(CO)$_4$ fragments (Mn(1)–Mn(2) = 2.7877(5) Å, Mn(1)–P(1) = 2.3216(4) Å, Mn(2)–P(1) = 2.2755(4) Å, P(1)–N(4) = 1.698(1) Å, C(4)–Mn(1)–Mn(2)–C(8) torsion angle = 10.10(6)°). The long P(1)–C(9) length of 1.870(1) Å



1 R = ^{t}Bu (**3**), adamantyl (**4**) R = ^{t}Bu (**5**), adamantyl (**6**)

Scheme 1

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† Electronic supplementary information (ESI) available: Full experimental and characterisation details for adducts **5–8**. See DOI: 10.1039/b604150g

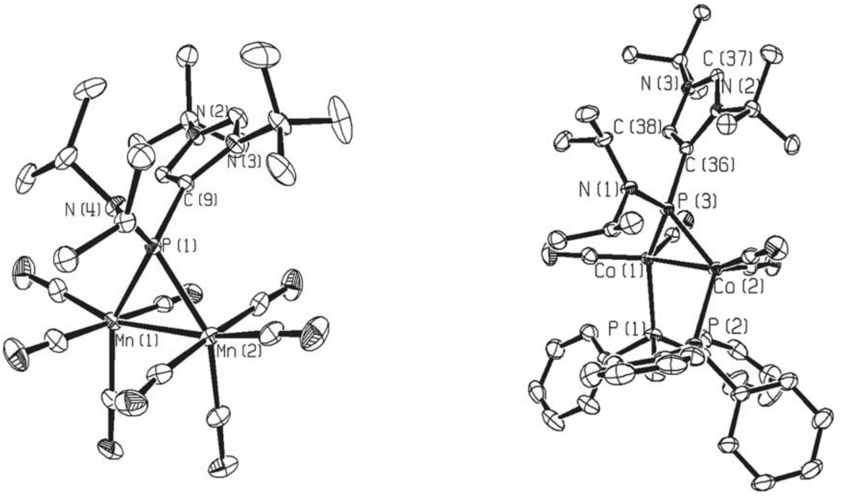
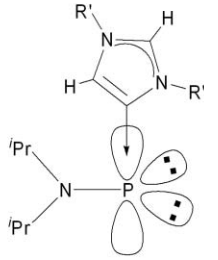


Fig. 1 ORTEP diagrams of compounds **5** (left) and **7** (right). Hydrogen atoms have been eliminated for clarity and thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (°): **5**: Mn(1)–Mn(2) 2.7877(5), Mn(1)–P(1) 2.3216(4), Mn(2)–P(1) 2.2755(4), P(1)–N(4) 1.698(1), P(1)–C(9) 1.870(1), Mn(1)–P(1)–Mn(2) 74.65(2), Mn(1)–P(1)–N(4) 125.02(4), Mn(1)–P(1)–C(9) 110.30(4), Mn(2)–P(1)–N(4) 123.33(4), Mn(2)–P(1)–C(9) 11.68; **7**: Co(1)–Co(2) 2.6835(4), Co(1)–P(3) 2.1584(5), Co(2)–P(3) 2.1298(5), Co(1)–P(1) 2.1739(5), Co(2)–P(2) 2.1774(5), P(3)–N(1) 1.7102(1), P(3)–C(36) 1.865(2), Co(1)–P(3)–Co(2) 77.48(2), Co(1)–P(3)–N(1) 123.76(5), Co(1)–P(3)–C(36) 112.04(5), Co(2)–P(3)–N(1) 123.92(5), Co(2)–P(3)–C(36) 121.07(5).

indicates that the interaction between these atoms is primarily donor–acceptor in nature (*cf.* P(3)–C(2a) = 1.737(2) Å in $[Co_2(CO)_6(\mu\text{-dppm})(\mu\text{-}\eta^1,\eta^2\text{-P(TMP)=CH}_2)]$[8] or 1.794(3) Å in 1,3,4,5-tetramethylimidazol-2-ylidene·phenylphosphinidene)[12] with little or no C–P π-bonding. The complex $[Mn_2(CO)_8\{\mu\text{-P(N}^i\text{Pr}_2)(4\text{-cyclo-C}_3\text{H}_2\text{-1,3-(NR)}_2)\}]$ (R = adamantyl (**6**)) was prepared similarly, and has an analogous structure.

The reaction of **2** with the NCN carbene **3** in THF results in the quantitative formation, over several days, of the new compound $[Co_2(CO)_4(\mu\text{-dppm})\{\mu\text{-P(N}^i\text{Pr}_2)(4\text{-cyclo-C}_3\text{H}_2\text{-1,3-(N}^t\text{Bu)}_2)\}]$ (**7**). As found in the reaction of **1** with **3**, no intermediates were observed during the reaction. The ^{31}P NMR spectrum of complex **7** shows a resonance at δ 254, and resonances for the dppm P atoms at δ 41 and 38. The non-equivalence of the latter two signals suggests that the NCN carbene is bound to the phosphinidene phosphorus *via* the 4-position of the carbene. The X-ray structure‡ of the THF solvate confirms this formulation, and the main structural features include a metal–metal-bonded, dppm-bridged complex (Co(1)–Co(2) = 2.6835(4) Å, Co(1)–P(1) = 2.1739(5) Å, Co(2)–P(2) = 2.1774(5) Å) with an elongated bond between the phosphinidene phosphorus and the NCN carbene (P(3)–C(36) = 1.865(2) Å). Complex **8** was prepared by the reaction of complex **2** with NCN carbene **4**, and has an analogous structure. Recently, we have described the synthesis of the related complexes $[Co_2(CO)_4(\mu\text{-dppm})\{\mu\text{-}\eta^1,\eta^2\text{-P(NR}_2)\text{=CH}_2\}]$ (NR$_2$ = N^{i}Pr$_2$ (**9**) and tetramethylpiperidyl (**10**)) *via* the reaction of μ-phosphinidene precursors with diazomethane.[8] Complexes **9** and **10** contain σ–π-phosphaalkene ligands, and provide an interesting comparison to complexes **7** and **8**. The P=C bond length in the phosphaalkene ligand of complex **10** is 1.737(2) Å, and is relatively long compared to typical phosphaalkenes (*cf.* 1.660(6) and 1.674(2) Å in *E*- and *Z*-Mes*P=C(H)Ph, respectively, where Mes* = 2,4,6-tri-*tert*-butylphenyl).[13] The elongation is most likely a result of the π-interaction between the P=C bond and the cobalt centre. As was observed for **5** and **6**, the much longer P–C bond length and the lack of a π-interaction with cobalt in complex **7** again suggests that the P–C (carbene) bond is a weak single bond.

In all four complexes **5–8**, the stereochemistry at the phosphorus atom is tetrahedral, with the N–P–C (carbene) plane perpendicular to the M$_2$P plane. An electron count indicates that the newly formed phosphorus ligands behave as 4-electron donors to the 34-electron binuclear M$_2$ core. These observations and the long P–C (carbene) bond lengths suggest that the NCN carbenes behave as Lewis bases, donating an electron pair into the vacant 3p orbital of the electrophilic coordinated phosphinidene in **1** and **2**, as in **B** below. Support for this bonding model comes from a concomitant reduction in π-bonding from the diisopropylamino group to the phosphinidene phosphorus, resulting in a lengthening of the P–N bond to 1.698(1) Å in **5** from 1.624(1) Å[8] in the precursor μ-phosphinidene complex **1**.



B

The complexes described above are the first reported examples of main group element adducts of abnormal carbene ligands. Crabtree *et al.* have reported cationic iridium complexes containing bidentate, pyridine-functionalized NCN carbene ligands that bind to the metal centre *via* the pyridyl nitrogen and the abnormal carbene position (C-4 in **A**, where R$_1$ = 2-pyridyl).[14] Calculations indicate that for free imidazolidene, the isomer with the carbene in the 2-position is 20 kcal mol^{-1} more stable than the isomer with the carbene located at the 4-position. When bound to a

$PtCl_3^-$ fragment, the difference is even more pronounced (ΔE = 23.3 kcal mol^{-1}).[15]

Although we are uncertain whether complexes **5–8** are kinetic or thermodynamic products, it seems likely that unfavourable steric interactions between the N-bound R groups of the NCN carbene and either the N^{i}Pr$_2$ moiety or the metal bound carbonyl ligands would destabilize an interaction between the phosphinidene phosphorus and the C-2 of the carbene. In support of this, we have found that heating a THF solution of complex **5** (80 °C for one week and 100 °C overnight) causes no observable change. It is possible that the energy difference between imidazol-2-ylidene and imidazol-4-ylidene results in a very low concentration of free 4-ylidene in solution. Steric hindrance may then drive the reaction to form the more thermodynamically-favourable isomers in reactions with μ-phosphinidene complexes.

In this study we have shown that the combination of a phosphinidene complex, derived from a singlet phosphinidene, with a free singlet carbene results in the donor group binding to the electrophilic, coordinated phosphorus centre. We have also unexpectedly found that the ylidene group has migrated from the 2- to the 4-position, forming abnormal carbene adducts of the phosphinidene complexes. The unusual nature of the highly reactive phosphinidene bridge in the μ-PR complexes should allow for the synthesis of a range of novel phosphorus-containing complexes.

This work was supported by the National Research Council of Canada and the Natural Sciences and Engineering Research Council of Canada (to A. J. C.).

Notes and references

‡ Crystallographic data for: **5**: $C_{25}H_{34}Mn_2N_3O_8P$, M = 645.40, monoclinic, $P2(1)/n$, a = 10.951(2), b = 15.968(2), c = 16.925(2) Å, β = 100.384(2)°, V = 2911.1(7) Å^3, T = 125(2) K, Z = 4, μ = 0.972 mm^{-1}, 8136 unique, R_{int} = 0.0277, 35996 total, $R_1[I > 2\sigma(I)]$ = 0.0268, R_w(all data) = 0.0712. CCDC 602520. **7**: $C_{52}H_{68}Co_2N_3O_{5.50}P_3$, M = 1033.86, triclinic, P-1, a = 11.287(1), b = 11.694(1), c = 20.738(2) Å, α = 89.924(1), β = 74.930(1), γ = 75.533(1)°, V = 2553.6(4) Å^3, T = 125(2) K, Z = 2, μ = 0.793 mm^{-1}, 14076 unique, R_{int} = 0.0224, 31811 total, $R_1[I > 2\sigma(I)]$ = 0.0346, R_w(all data) = 0.0997. The co-crystallized THF molecules are disordered between six positions with site occupancies ranging from 0.13 to 0.43. All distances and angles within each THF molecule have been fixed, and for most THF molecules it is not possible to distinguish between oxygen and carbon. The structure has been refined without H-atoms on the THF molecules. CCDC 602521. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b604150g

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