Reactivity of electrophilic μ-phosphinidene complexes with heterocumulenes: formation of the first σ-π-aminophosphaimine complexes $[Mn_2(CO)_8\{\mu\text{-}\eta^1,\eta^2\text{-}P(N^iPr_2){=}NR\}]$ and diazoalkane insertions into metal–phosphorus bonds†

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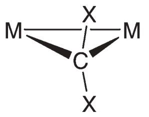
The bridging phosphinidene complexes $[Mn_2(CO)_8(\mu\text{-}PN^iPr_2)]$ and $[Co_2(CO)_4(\mu\text{-dppm})(\mu\text{-}PNR_2)]$ (NR_2 = N^iPr_2, TMP) react with heterocumulenes RN_3, CH_2N_2 and $Ph_2C{=}N{=}N$ to form complexes with μ-η^1,η^2-aminophosphaimine, μ-η^1,η^2-aminophosphaalkene and μ-η^1,η^2-aminophosphadiphenylmethylazaimine ligands, respectively.

Carbene (CX_2) and phosphinidene (PX) ligands are isolobal[1] and there are now well-established structure, bonding, and reactivity similarities[1,2] between, for example, Schrock type carbene complexes and their nucleophilic η^1-phosphinidene counterparts.[3] More recently the isolation of thermally stable, terminal electrophilic phosphinidenes of the mid[4] to late[5] transition metals has stimulated interest in the chemistry of these Fischer type molecules to complement the extensive knowledge of the reaction manifolds for transient phosphinidenes.[6]

Although bridging carbenes (μ-alkylidenes)[7] comprise an important and diverse class of organometallic molecules and intermediates, their μ-PX counterparts are relatively rare and their chemistry is virtually unexplored.[8,9] There are also structural and electronic differences between μ-CX_2 and μ-PX complexes: whereas bridging carbenes are formally saturated with tetrahedral stereochemistry at carbon as in I, in the latter, II, the phosphorus centre is planar and unsaturated,[10] and reactivity may be initiated by attack at the electrophilic phosphorus atom.



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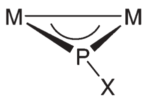

II

In this communication we describe the synthesis of two new examples of the class of μ-phosphinidene complexes, $[Mn_2(CO)_8(\mu\text{-}PN^iPr_2)]$ (**1**) and $[Co_2(CO)_4(\mu\text{-dppm})(\mu\text{-}PN^iPr_2)]$ (**2a**) and their novel reactions with heterocumulenes RN_3 (R = Me_3Si, Me_3Sn, Ph, adamantyl) and diazoalkanes (CH_2N_2, $Ph_2C{=}N{=}N$) which afford the first complexes of σ,π-bound aminophosphaimines $[Mn_2(CO)_8\{\mu\text{-}\eta^1,\eta^2\text{-}P(N^iPr_2){=}NR\}]$ (**3a–d**) and rare σ-π-aminophosphaalkene ligands $[Co_2(CO)_4(\mu\text{-dppm})(\mu\text{-}\eta^1,\eta^2\text{-}PNR_2{=}CH_2)]$ (NR_2 = N^iPr_2 (**4a**), TMP (**4b**)). Diphenyldiazomethane $Ph_2C{=}N{=}N$ also inserts into one arm of the phosphinidene bridge in **1** without loss of dinitrogen to yield the novel complex $[Mn_2(CO)_8\{\mu\text{-}P(N^iPr_2){=}N\text{–}N({=}CPh_2)\}]$ (**5**) which contains a Mn_2PN_2 five-membered ring.

The complex $[Mn_2(CO)_8(\mu\text{-}PN^iPr_2)]$ (**1**) was readily prepared by the reaction of $K[Mn(CO)_5]$ with $Cl_2PN^iPr_2$. This compound is surprisingly stable and persists for days in THF solution, whereas the related complexes $[Co_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PNR_2)]$ (NR_2 = N^iPr_2, TMP) readily lose carbonyl ligands and undergo condensation reactions to form the cluster complexes $[Co_4(CO)_8(\mu\text{-}CO)\{\mu_3\text{-}PNR_2\}_2]$ (NR_2 = TMP, N^iPr_2).[8] Complex **1** has a ^{31}P NMR resonance at δ 731, the downfield chemical shift of which is typical for bridging phosphinidene ligands.[8] The X-ray structure‡ shows a pseudooctahedral ligand arrangement about each manganese centre and a bridging aminophosphinidene ligand across the two metal centres (Mn(1)–Mn(2) = 2.9193(4) Å).

The reaction of **1** with organic azides RN_3 (R = Me_3Si, Me_3Sn, Ph, adamantyl) readily affords the complexes $[Mn_2(CO)_8\{\mu\text{-}\eta^1,\eta^2\text{-}P(N^iPr_2){=}NR\}]$ (R = Me_3Si (**3a**), Me_3Sn (**3b**), Ph (**3c**), adamantyl (**3d**)). The ^{31}P NMR spectrum of **3a** has a resonance at δ 216 and the ^1H NMR spectrum shows the presence of both ^iPr and Me_3Si groups. The X-ray structure of **3a**‡ (Fig. 1) shows that oxidation of the phosphinidene phosphorus has occurred with the formation of a novel μ-η^1,η^2-aminophosphaimine ligand. The phosphorus atom of the phosphaimine is bonded to Mn(2) (Mn(2)–P(1) = 2.1857(3) Å) with an elongated P=N bond (P(1)–N(2) = 1.5756(9) Å) coordinated in π-fashion to Mn(1) (Mn(1)–P(1) = 2.4084(3) Å, Mn(1)–N(2) = 2.1717(9) Å). To our knowledge this is the first example of a phosphaimine bound in typical μ-alkenyl fashion in a binuclear complex, although free phosphaimines have been previously characterised.[12]

Complexes that are isoelectronic to **3a–d** were produced in the reaction of $[Co_2(CO)_6(\mu\text{-dppm})(\mu\text{-}PNR_2)]$ (NR_2 = N^iPr_2 (**2a**), TMP (**2b**)) with CH_2N_2. The ^{31}P NMR spectrum of the product (NR_2 = N^iPr_2 (**4a**)) shows a new resonance at δ 247 and two resonances for the μ-dppm group at δ 46 and 38. The ^{13}C NMR spectrum of **4a** shows a resonance for the CH_2 fragment of the phosphaalkene ligand appearing as a broad signal at δ 24. The X-ray structure of **4b**‡ (Fig. 1) shows that insertion of methylene into a Co–P bond of **2b** has occurred with loss of N_2 and the

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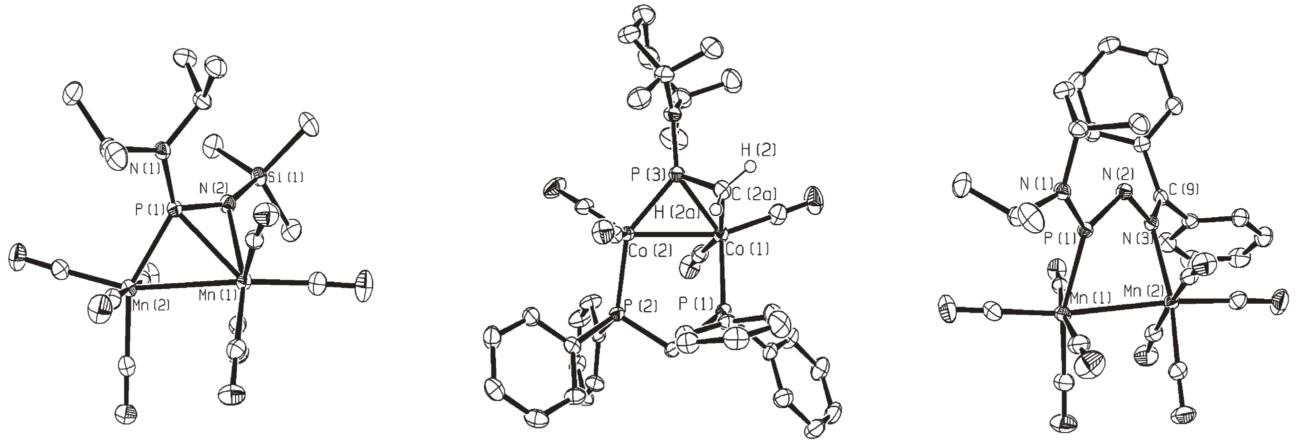
† Electronic supplementary information (ESI) available: Synthetic and spectroscopic data for compounds **1**, **3a–d**, **4a–b**, **5**; crystallographic details for compounds **1**, **3a**, **3c**, **4b**, and **5**. See http://dx.doi.org/10.1039/b505472a

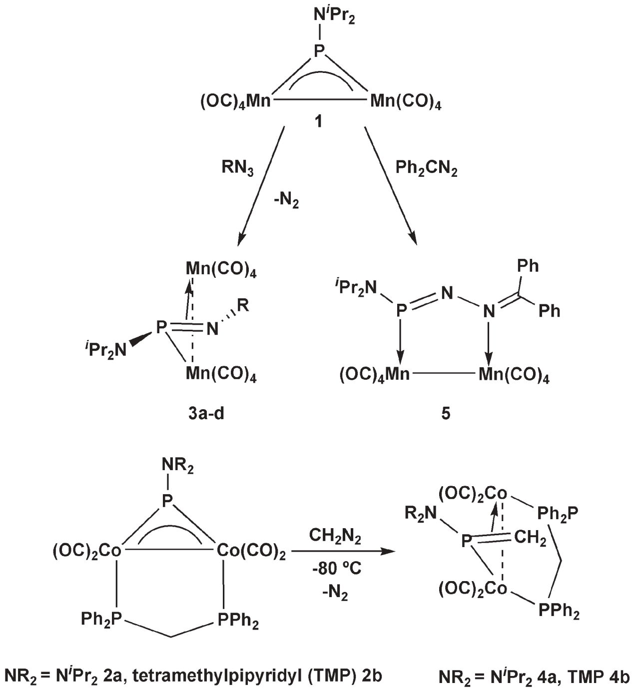


3a **4b** **5**

Fig. 1 ORTEP diagrams of compounds **3a**, **4b** and **5**. Selected hydrogen atoms have been eliminated for clarity and thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (°): **3a**: Mn(1)–Mn(2) 2.8888(3), Mn(1)–P(1) 2.4084(3), Mn(1)–N(2) 2.1717(9), Mn(2)–P(1) 2.1857(3), P(1)–N(1) 1.6512(9), P(1)–N(2) 1.5756(9), N(2)–Si(1) 1.7297(9), Mn(2)–P(1)–N(1) 128.69(3), Mn(2)–P(1)–N(2) 118.04(4), Mn(1)–P(1)–Mn(2) 77.76(1), Mn(1)–P(1)–N(1) 126.23(4), Mn(1)–P(1)–N(2) 61.97(3), N(2)–P(1)–N(1) 113.15(5); **4b**: Co(1)–Co(2) 2.7143(5), Co(1)–P(1) 2.2135(6), Co(1)–P(3) 2.1321(6), Co(2)–P(2) 2.1948(6), Co(2)–P(3) 2.1232(6), Co(1)–C(2a) 2.105(2), N(1)–P(3) 1.669(2), P(3)–C(2a) 1.737(2), Co(1)–P(3)–Co(2) 79.27(2), Co(2)–P(3)–C(2a) 108.92(8), Co(1)–P(3)–C(2a) 64.98(7); **5**: Mn(1)–Mn(2) 2.8945(4), Mn(1)–P(1) 2.1845(5), Mn(2)–N(3) 2.103(1), P(1)–N(1) 1.631(1), P(1)–N(2) 1.593(1), N(2)–N(3) 1.418(2), Mn(1)–P(1)–N(1) 127.71(5), Mn(1)–P(1)–N(2) 125.49(5), N(1)–P(1)–N(2) 106.69(7).

formation of a new μ-η^1,η^2-coordinated aminophosphaalkene complex. The principal structural features are a short Co–Co bond (Co(1)–Co(2) 2.7143(5) Å) and a coordinated phosphaalkene (TMP)P=CH$_2$ bound to Co(2) *via* phosphorus and to Co(1) in π-fashion *via* the P=C bond (P(3)–C(2a) = 1.737(2) Å). The P=C bond length is comparable to that in [Cp$_2$Mo$_2$(CO)$_4$(μ,η^1,η^2–P(Ph)=CHMe)], a similar phosphaalkene complex synthesized *via* an entirely different route by Mays and co-workers.[11] The methine carbon resonance of the CHMe group in [Cp$_2$Mo$_2$(CO)$_4$(μ-η^1,η^2-P(Ph)=CHMe)] appears at δ 42 and is similar to the =CH$_2$ resonance in **4a**. Although the ^{13}C chemical shift of C(2a) is more indicative of an sp^3 hybridized carbon atom, the short P(3)–C(2a) bond length is consistent with a metal coordinated phosphaalkene. We are unaware of any other examples of this class of molecule.

The reaction of **1** with diphenyldiazomethane (Scheme 1) affords a species with a ^{31}P NMR resonance at δ 285. Although the ^{1}H NMR spectrum of **5** shows the presence of both Ph and ^{i}Pr groups, it was necessary to carry out an X-ray crystallographic study to determine if the N$_2$ fragment of the diazoalkane was retained.‡ The structure (Fig. 1) shows that the diazoalkane has inserted into one Mn–P bond without N$_2$ extrusion to form a five-membered Mn$_2$PN$_2$ ring. The dimetallacycle has a puckered conformation which results in a staggered arrangement for the three carbonyl ligands on each metal that are perpendicular to the metal–metal bond. The geometry about each metal centre is pseudooctahedral with a Mn(1)–P(1) separation of 2.1845(5) Å and a Mn(2)–N(3) bond length of 2.103(1) Å. While the stereochemistry about P(1) is trigonal planar, the P(1)–N(1) distance to the diisopropylamino group (1.630(1) Å) is distinctly longer than P(1)–N(2) (1.593(1) Å) and together with the short N(2)–N(3) bond (1.418(2) Å) indicates a significant π-character in the PN$_2$ portion of the metallacycle. However the P(1)–N(2) bond is slightly longer than the P=N separation of 1.545(2) Å in the free phosphaimine (Me$_3$Si)$_2$NP=NSiMe$_3$[12] but is similar to the PN bond length in the nickel cluster [Ni$_4$(CN^{t}Bu)$_4$(μ$_3$-η^2-CN^{t}Bu)(μ$_3$-η^2-(Me$_3$Si)$_2$NP=NSiMe$_3$)$_2$].[13]



Scheme 1

While the reaction of **2** with CH$_2$N$_2$ and **1** with Ph$_2$CN$_2$ both lead to insertion into the phosphinidene bridge, complex **5** is formed without extrusion of N$_2$ from the diazoalkane whereas in **4b** loss of N$_2$ has afforded a phosphaethene ligand. Attempts to convert **5** thermally to the corresponding phosphadiphenylethylene complex (80 °C, C$_6$D$_6$, overnight) resulted in decomposition.

In conclusion, these results confirm that doubly bridging phosphinidene complexes, like their μ-alkylidene counterparts[14] are highly susceptible to insertion reactions with unsaturated substrates. The electrophilic, unsaturated nature of the μ-PR bridge appears to be only partially alleviated by the presence of the electron donating NR_2 group and through back donation from the metal centres. The reactivity of the PR bridge presents a wealth of new opportunities for the synthesis of novel phosphorus ligands.

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Notes and references

‡ Crystallographic data for: **1** $[C_{14}H_{14}Mn_2NO_8P]$, $M = 465.11$, triclinic, $P\bar{1}$, $a = 6.6736(7)$ Å, $b = 9.5035(9)$ Å, $c = 15.4285(15)$ Å, $\alpha = 104.344(2)°$, $\beta = 96.656(2)°$, $\gamma = 97.440(2)°$, $V = 928.81(16)$ Å^3, $T = 125(2)$ K, $Z = 2$, $\mu = 1.486$, 5109 unique, $R_1[I > 2\sigma(I)] = 0.0232$, R_w (all data) = 0.0633. CCDC 275485. **3a**: $[C_{17}H_{23}Mn_2N_2O_8PSi]$, $M = 552.31$, monoclinic, $P2_1/c$, $a = 15.7307(13)$ Å, $b = 10.5029(8)$ Å, $c = 15.5917(13)$ Å, $\alpha = 90°$, $\beta = 113.0100(10)°$, $\gamma = 90°$, $V = 2371.1(3)$ Å^3, $T = 125(2)$ K, $Z = 4$, $\mu = 1.226$, 5835 unique, $R1[I > 2\sigma(I)] = 0.0198$, R_w (all data) = 0.0543. CCDC 275484. **3c**: $[C_{20}H_{19}Mn_2N_2O_8P]$, $M = 556.22$, monoclinic, $P2_1/c$, $a = 8.8228(11)$ Å, $b = 9.7766(12)$ Å, $c = 28.072(3)$ Å, $\alpha = 90°$, $\beta = 97.045(2)°$, $\gamma = 90°$, $V = 2403.1(5)$ Å^3, $T = 125(2)$ K, $Z = 4$, $\mu = 1.164$, 6717 unique, $R_1[I > 2\sigma(I)] = 0.0236$, R_w (all data) = 0.0634. CCDC 275483. **4b**: $[C_{39}H_{42}Co_2NOP_3]$, $M = 799.51$, monoclinic, $C2/c$, $a = 30.170(6)$ Å, $b = 10.6655(19)$ Å, $c = 23.493(4)$ Å, $\alpha = 90°$, $\beta = 102.347(3)°$, $\gamma = 90°$, $V = 7385(2)$ Å^3, $T = 125(2)$ K, $Z = 8$, $\mu = 1.070$, 10308 unique, $R_1[I > 2\sigma(I)] = 0.0347$, R_w (all data) = 0.0914. CCDC 269680. **5**: $[C_{29}H_{29}Mn_2N_3O_{8.5}P]$, $M = 696.40$, monoclinic, $P2_1/c$, $a = 12.1027(16)$ Å, $b = 20.563(3)$ Å , $c = 13.6644(18)$ Å , $\alpha = 90°$, $\beta = 111.888(2)°$, $\gamma = 90°$, $V = 3155.5(7)$ Å^3, $T = 125(2)$ K, $Z = 4$, $\mu = 0.905$, 7871 unique, $R_1[I > 2\sigma(I)] = 0.0322$, R_w (all data) = 0.0887. CCDC 269679. See http://dx.doi.org/10.1039/b505472a for crystallographic data in CIF or other electronic format.

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