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Reactivity patterns of thermally stable, terminal, electrophilic phosphinidene complexes towards diazoalkanes: oxidation at the phosphorus centre and formation of P-bound η^1-phosphaazine, η^1-phosphaalkene and η^3-diazaphosphaallene complexes†

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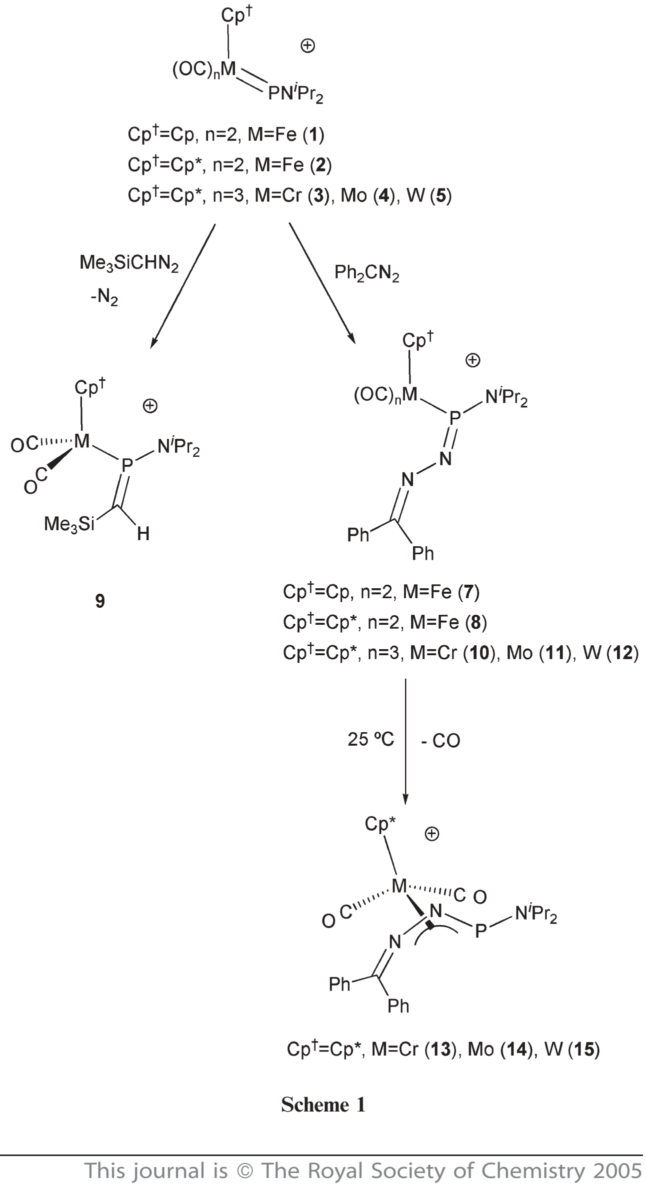
The thermally stable, terminal phosphinidene complexes $[Cp^{\dagger}M(CO)_2(\eta^1\text{-}PN^iPr_2)]AlCl_4$ ($Cp^{\dagger}$ = Cp, Cp*; M = Fe) and $[Cp^*M(CO)_3(\eta^1\text{-}PN^iPr_2)]AlCl_4$ (M = Cr, Mo, W) react with $Ph_2C{=}N{=}N$ to form terminal P-coordinated η^1-phosphaazine and η^3-diazaphosphaallene ligands, respectively, whereas $[CpFe(CO)_2(\eta^1\text{-}PN^iPr_2)]AlCl_4$ reacts with Me_3SiCHN_2 affording a terminal phosphorus bound η^1-phosphaalkene complex.

Since the isolation and structural characterisation of the first thermally stable, cationic, terminal phosphinidene complexes in 2001,[1] studies of the reactivity patterns of these interesting analogues of Fischer carbenes have become possible. Reactions reported to date include: nucleophilic attack at the electrophilic P(I) centre by phosphines and diphosphines forming P–P bonds;[2,3] addition of alkynes and alkenes generating P-coordinated[4] (or olefin bound[5]) phosphirenes or phosphiranes; addition of activated HX (X = SiR_3, OR, $C_6H_4N_2Ph$)[3,6] bonds affording coordinated functionalized phosphine ligands. In this communication we report a further class of novel reactions with diazoalkanes which effectively result in oxidation at the phosphinidene centre to generate novel unsaturated phosphorus(III) ligands which are planar at phosphorus: η^1-phosphaazines, η^1-phosphaalkenes, and η^3-bound diazaphosphaallenes. These transformations provide further confirmation that terminal, electrophilic phosphinidene complexes possess an exciting and diverse chemistry.

Herein we describe the synthesis of the new complex $[Cp^{\dagger}Fe(CO)_2(\eta^1\text{-}PN^iPr_2)]AlCl_4$ ($Cp^{\dagger}$ = Cp (**1**)) and the reactivity of **1** and **2** ($Cp^{\dagger}$ = Cp* (**2**)) and the related complexes $[Cp^*M(CO)_3(\eta^1\text{-}PN^iPr_2)]AlCl_4$ (M = Cr (**3**), Mo (**4**), W (**5**))[1] towards the diazoalkanes Ph_2CN_2 and Me_3SiCHN_2. The reaction of **1** or **2** with Ph_2CN_2 selectively produces complexes containing η^1-phosphaazine ligands whereas the addition of Me_3SiCHN_2 to **1** instead forms an η^1-phosphaalkene complex. The addition of Ph_2CN_2 to **3–5** results in the formation of complexes containing novel η^3-diazaphosphaallene ligands. While the reactivity of carbene complexes towards diazoalkanes has been studied extensively with respect to carbon–carbon bond formation,[7] to the best of our knowledge there have been no reports on the analogous chemistry with transient[8] or stable[1–5] terminal phosphinidene complexes. These results complement recent evidence that bimetallic μ-phosphinidene complexes such as $[Mn_2(CO)_8(\mu\text{-}PN^iPr_2)]$ react with diazoalkanes and azides to afford bridging, σ–π unsaturated phosphorus ligands.[9]



Scheme 1

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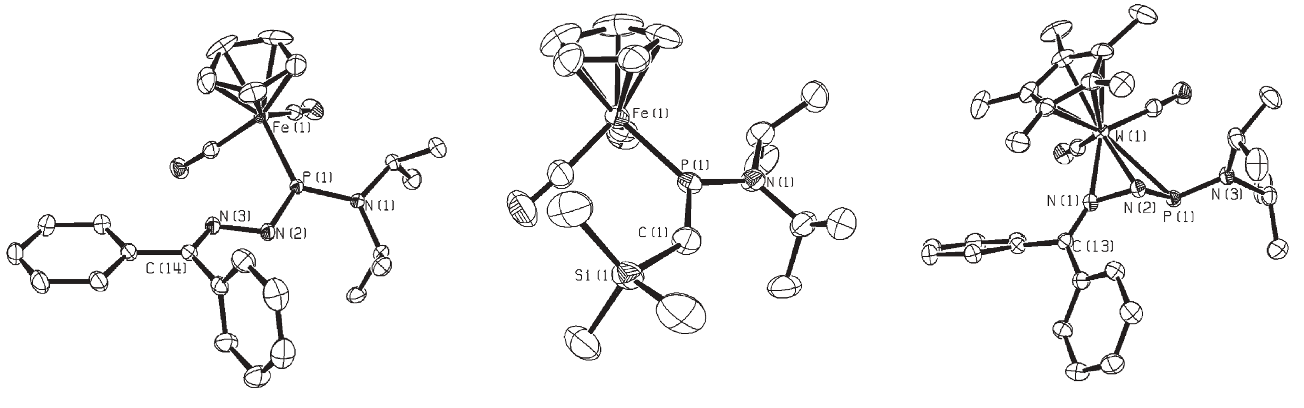

7

9

15

Fig. 1 ORTEP diagrams of the cations of compounds **7**, **9** and **15**. Only the major component of compound **9** is shown. Hydrogen atoms have been eliminated for clarity and thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (°): **7**: Fe(1)–P(1) 2.1691(4); P(1)–N(1) 1.624(1); P(1)–N(2) 1.575(1); N(2)–N(3) 1.403(2); N(3)–C(14) 1.296(2); Fe(1)–P(1)–N(1) 126.19(4); Fe(1)–P(1)–N(2) 124.59(4); P(1)–N(2)–N(3) 114.45(9). **9**: Fe(1)–P(1) 2.2135(8); 2.2135(8); P(1)–C(1) 1.633(3); P(1)–N(1) 1.641(2); Si(1)–C(1) 1.862(3); Fe(1)–P(1)–N(1) 119.80(8); Fe(1)–P(1)–C(1) 126.3(1); P(1)–C(1)–Si(1) 138.4(2). **15**: W(1)–P(1) 2.7289(9); W(1)–N(1) 2.076(2); W(1)–N(2) 2.201(2); P(1)–N(2) 1.704(2); P(1)–N(3) 1.642(2); N(1)–N(2) 1.424(3); N(2)–N(3) 1.403(2); N(1)–C(13) 1.294(3); W(1)–P(1)–N(2) 53.70(7); W(1)–P(1)–N(3) 111.78(8); W(1)–N(2)–P(1) 87.69(8); W(1)–N(1)–N(2) 75.4(1); W(1)–N(2)–N(1) 65.9(1); W(1)–N(1)–C(13) 155.9(2); N(1)–N(2)–P(1) 102.1(1); N(2)–N(1)–C(13) 126.3(2).

The complex $[CpFe(CO)_2(\eta^1\text{-}PN^iPr_2)]AlCl_4$ (**1**) which has been fully characterised was prepared *via* $AlCl_3$ induced halide abstraction from the phosphide precursor $[CpFe(CO)_2(\eta^1\text{-}P(Cl)N^iPr_2)]$ (**6**). A resonance appears in the ^{31}P NMR spectrum of **1** at δ 922, similar to that of the structurally characterised analogue $[Cp^*Fe(CO)_2(\eta^1\text{-}PN^iPr_2)]AlCl_4$ (δ 965).[10]

The addition of Ph_2CN_2 to **1** (Scheme 1) rapidly affords a complex containing an η^1-coordinated phosphaazine ligand $[CpFe(CO)_2\{\eta^1\text{-}P(N^iPr_2){=}N{-}N{=}(CPh_2)\}]AlCl_4$ (**7**). The ^{31}P NMR spectrum of **7** exhibits a resonance at δ 291 Hz. The X-ray structure‡ (Fig. 1) shows that the phosphaazine ligand is η^1-bound to iron *via* phosphorus (Fe–P(1) = 2.1691(4) Å) and that the N^iPr_2 and $NCPh_2$ substituents have a *trans* disposition with respect to the P=N double bond (P(1)–N(2) = 1.575(1) Å). The complex $[Cp^*Fe(CO)_2\{\eta^1\text{-}P(N^iPr_2){=}N{-}N(CPh_2)\}]AlCl_4$ (**8**) prepared in the same manner has a similar structure.

The addition of the diazoalkane Me_3SiCHN_2 to **1** proceeds with vigorous gas evolution to afford the η^1-phosphaalkene complex $[CpFe(CO)_2\{\eta^1\text{-}P(N^iPr_2){=}CHSiMe_3\}]AlCl_4$ (**9**) (δ ^{31}P 241). The ^1H NMR spectrum of **9** shows a resonance for the $=CH$ signal at δ 6.43 and the relatively large $^2J_{PH}$ coupling of 36.8 Hz strongly suggests that N_2 has been lost during the reaction with the formation of a P=C bond. This is confirmed by the X-ray structure‡ (Fig. 1). The major structural features include a typical piano-stool ligand arrangement about the iron atom and a Fe–P(1) separation of 2.2135(8) Å. The bulky N^iPr_2 and $SiMe_3$ groups are in the expected *trans* positions about the P=C double bond (P(1)–C(1) = 1.633(3) Å; P(1)–N(1) = 1.641(2) Å). Attempts to convert **7** into a phosphaalkene complex similar to **9** (70 °C overnight) *via* loss of N_2 resulted only in decomposition.

When Ph_2CN_2 was added to $[Cp^*W(CO)_3(\eta^1\text{-}PN^iPr_2)]AlCl_4$ (**5**) the immediate evolution of gas was also observed, together with the formation of a complex with a ^{31}P NMR resonance at δ 125. An X-ray structure determination‡ established the presence of a novel diazaphosphaallene ligand η^3-coordinated to the tungsten atom in $[Cp^*W(CO)_2\{\eta^3\text{-}P(N^iPr_2)NNCPh_2\}]AlCl_4$ (**15**) and confirmed the loss of CO from **5**. The diazaphosphaallene ligand is oriented in an *exo* fashion with W–N(1) and N(2) separations of 2.076(2) Å and 2.201(2) Å, respectively. The W–P(1) bond length (2.7289(9) Å) is lengthened significantly compared to the W=P separation in **5** (2.4503(6) Å)[1] indicating that the phosphorus atom of the η^3-diazaphosphaallene ligand is rather weakly bound to the metal centre. To our knowledge this is the first diazaphosphaallene complex to be described although a related molecule $[CpMo(CO)_2(\eta^3\text{-}P(^tBu)PC(SiMe_3)_2)]$ containing a diphosphaallyl ligand recently described by Weber and co-workers has a similar Mo–P(2) separation of 2.6756(3) Å.[11] Since the reactivity of thermally stable, electrophilic phosphinidene complexes is typically initiated by binding of nucleophilic substrates to the vacant p-orbital on phosphorus,[2] we believe that the addition of Ph_2CN_2 to **5** results in the initial formation of adduct **12** which then subsequently undergoes CO loss to form η^3-diazaphosphaallene complex **15**. Although **12** has not been observed spectroscopically, the isolation and structural characterisation of complex **7** strongly supports the proposed mechanism. Analogues $[Cp^*M(CO)_2\{\eta^3\text{-}P(N^iPr_2)NN(CPh_2)\}]AlCl_4$ (M = Cr (**13**); Mo (**14**)) were prepared similarly.

In conclusion, we have shown that terminal electrophilic phosphinidene ligands may be converted into η^1-phosphaazine, η^1-phosphaalkene and η^3-diazaphosphaallene ligands. The highly reactive nature of the phosphinidene complexes allows for the synthesis of a wide range of phosphorus-containing ligands that are difficult or impossible to obtain using standard synthetic protocols.

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Notes and references

‡ Crystallographic data for: **7** $[C_{27}H_{31}AlCl_6FeN_3O_2P]$, 756.05, monoclinic, $P2_1/c$, a = 10.3584(8) Å, b = 17.449(1) Å, c = 18.948(2) Å, β = 99.531(1)°,

V = 3377.5(5) Å^3, T = 125(2) K, Z = 4, μ = 1.025 mm^{-1}, 9406 unique, $R1$ [$I > 2\sigma(I)$] = 0.0286, R_w(all data) = 0.0780. Note: in the crystal the Cp ring is disordered over two positions with 90% and 10% occupancies. **9** [$C_{17}H_{29}AlCl_4FeNO_2PSi$], 563.10, monoclinic, $P2_1$, a = 10.7258(7) Å, b = 11.0115(7) Å, c = 11.2248(7) Å, β = 90.9410(10)°, V = 1325.6(2) Å^3, T = 125(2), Z = 2, μ = 1.124 mm^{-1}, 6824 unique, R_1 [$I > 2\sigma(I)$] = 0.0374, R_w(all data) = 0.1018. Note: in the crystal the molecule is disordered over two sites with an occupancy of 87% and 13%. The structure was first refined with the same anisotropic thermal parameters for equivalent atoms in each disordered part. The site occupancies were found to be 0.87 and 0.13; these were then fixed at 0.87 and 0.13 and the structure was refined again. The $AlCl_4$ counterion was disordered over three sites. **15** [$C_{32}H_{41}AlCl_6N_3O_2PW$], 954.18, monoclinic, $P2_1/c$, a = 11.615(3) Å, b = 14.159(4) Å, c = 24.833(6) Å, β = 105.26(1)°, V = 3939.9(18) Å^3, T = 125(2) K, Z = 4, μ = 3.434 mm^{-1}, 9769 unique, R_1 [$I > 2\sigma(I)$] = 0.0251, R_w(all data) = 0.0674. CCDC 283075–283077. For crystallographic data in CIF or other electronic format see DOI: /10.1039/b512375e/

1 B. T. Sterenberg, K. A. Udachin and A. J. Carty, *J. Organomet. Chem.*, 2001, **617**, 696; B. T. Sterenberg, K. A. Udachin and A. J. Carty, *Organometallics*, 2001, **20**, 2657.

2 B. T. Sterenberg, K. A. Udachin and A. J. Carty, *Organometallics*, 2001, **20**, 4463.

3 T. W. Graham, K. A. Udachin and A. J. Carty, *Organometallics*, 2005, **24**, 2023.

4 J. Sánchez-Nieves, B. T. Sterenberg, K. A. Udachin and A. J. Carty, *J. Am. Chem. Soc.*, 2003, **125**, 2404.

5 R. Waterman and G. L. Hillhouse, *Organometallics*, 2003, **22**, 5182.

6 B. T. Sterenberg, J. Sánchez-Nieves and A. J. Carty, to be published.

7 C. P. Casey, S. H. Bertz and T. J. Burkhardt, *Tetrahedron Lett.*, 1973, **16**, 1421.

8 J. B. M. Wit, G. T. van Eijkel, F. J. J. de Kanter, M. Schakel, A. W. Ehlers, M. Lutz, A. L. Spek and K. Lammertsma, *Angew. Chem., Int. Ed.*, 1999, **38**, 2596; N. H. Tran Huy and F. Mathey, *J. Org. Chem.*, 2000, **65**, 652; K. Lammertsma, *Top. Curr. Chem.*, 2003, **229**, 95; F. Mathey, N. H. Tran Huy and A. Marinetti, *Helv. Chim. Acta*, 2001, **84**, 2938; K. B. Dillon, F. Mathey and J. F. Dixon, *Phosphorus: The Carbon Copy*, John Wiley & Sons Ltd., Chichester, UK, 1998.

9 T. W. Graham, K. A. Udachin and A. J. Carty, *Chem. Commun.*, 2005, 35, 4441.

10 B. T. Sterenberg, K. A. Udachin and A. J. Carty, *Organometallics*, 2003, **22**, 3927.

11 L. Weber, G. Noveski, U. Lassahn, H.-G. Stammler and B. Neumann, *Eur. J. Inorg. Chem.*, 2005, 1940.