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Synthesis, characterisation and reactivity of a novel iridaphosphirene complex, [Ir{=C(Bu^t)P(Cy)}(CO)(PPh$_3$)$_2$], Cy = cyclohexyl

Markus Brym, Cameron Jones* and Anne F. Richards

Department of Chemistry, University of Wales, Cardiff, P.O. Box 912, Park Place, Cardiff, UK CF10 3TB. E-mail: jonesca6@cardiff.ac.uk

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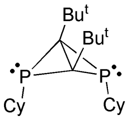
The reaction of the phosphavinyl Grignard reagent, [CyP=C(Bu^t)MgCl(OEt$_2$)], Cy = cyclohexyl, with Vaska's compound affords the first example of an iridaphosphirene complex, [Ir{=C(Bu^t)P(Cy)}(CO)(PPh$_3$)$_2$], which has been crystallographically characterised and its reaction with CO examined.

Since our development of a high yielding synthetic route to a range of phosphavinyl Grignard reagents, *e.g.* *Z*-[CyP=C(Bu^t)MgCl(OEt$_2$)] **1**,[1] we have systematically explored the use of such compounds as transfer reagents in reactions with main group halide complexes. These reactions can lead to terminal phosphavinyl-metal complexes, *e.g.* [Me$_2$Sn{C(Bu^t)=PCy}$_2$],[2] but generally phosphavinyl coupling reactions occur to give novel strained metallocage or heterocyclic compounds, *e.g.* [Bu^{t}C(μ-PCy)$_2${μ-AlC(Bu^t)=PCy}CBu^t].[3] In this respect, the chemistry of **1** is significantly different to normal vinyl Grignard reagents. More recently, we have made efforts to extend this study to the formation of transition metal-phosphavinyl complexes though this has proven problematic as the variable accessible oxidation states of transition metals generally leads to facile oxidative coupling of the phosphavinyl fragment to give either the 2,4-diphosphabicyclo[1.1.0]butane, **2**, or its 1,2-dihydro-1,2-diphosphete valence isomer.[4] It is noteworthy that in the reaction of Cp*TaCl$_4$ with **1** we managed to isolate an intermediate in the formation of **2**, namely the 4e$^-$-λ^3-diphosphinocarbene complex, **3**, which could alternatively be formulated as an η^2-4e$^-$-λ^5-diphosphaalkyne complex.[5] This complex is, however, thermally unstable in solution above −50 °C. We wished to prepare more stable complexes derived from **1** and believed precursors with the transition metal in a low oxidation state, *e.g.* Vaska's compound, would be more suited to this purpose. Herein we report the preliminary results of this investigation.



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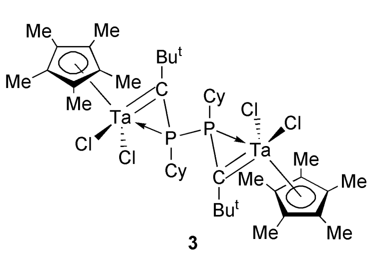

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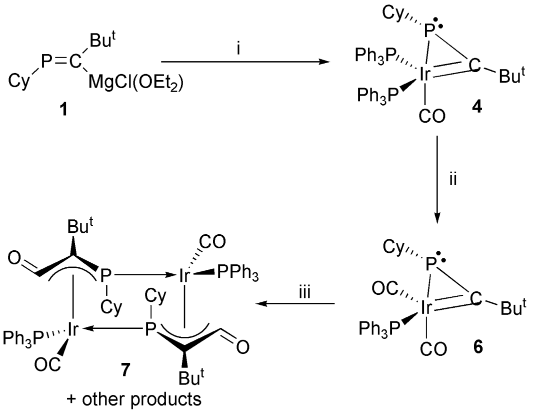
The reaction of [IrCl(CO)(PPh$_3$)$_2$] with one equivalent of **1** led to a moderate yield of **4** (51%) after recrystallisation from toluene (Scheme 1). Compound **4** can be considered as an 18-electron complex containing a three-membered iridaphosphirene ring in which the iridium centre is coordinated by a 3e$^-$-phosphidocarbene ligand. An alternative formulation for this ligand would have it acting as a 3e$^-$-η^2-phosphavinyl fragment within a Ir–C=P three-membered ring but the spectroscopic and crystallographic evidence suggests this is not the case (*vide infra*). Crystallographically authenticated metallaphosphirene complexes with the phosphorus centre in the +3 oxidation state are rare but, unlike **4**, those that have been reported are all derived from the earlier transition metals, *e.g.* [Cp(CO)$_2$W=C(Ph)–P(Ph){η^1-W(CO)$_5$}] **5**[6] and [Tp′(CO)$_2$W=C(H)–PC(NEt$_2$)$_2$][SO$_3$CF$_3$], Tp′ = HB(3,5-Me$_2$C$_3$HN$_2$)$_3$.[7] Interestingly, the three-membered ring within **4** is related to those in **3** and related complexes, *e.g.* [Cp*H$_2$Ta{=C(H)–PMe$_2$}(PMe$_3$)],[8] but in those cases the carbene ligands are 4e$^-$-donors.



Scheme 1 Reagents and conditions: i, IrCl(CO)(PPh$_3$)$_2$, C$_7$H$_8$, −MgCl$_2$; ii, CO, −PPh$_3$; iii, 25 °C, 5 hours, C$_7$H$_8$.

The spectroscopic data † for **4** support its proposed structure. Its ^{31}P{^{1}H} NMR spectrum exhibits a signal at high field (−157.2 ppm, *cf.* −188.7 ppm for **5**) that corresponds to the iridaphosphirene P-centre and is coupled to both PPh$_3$ phosphorus atoms ($^2J_{PP}$ = 22 and 66 Hz). If the compound existed as an η^2-phosphavinyl complex this signal would be expected to appear at considerably lower field. In addition the carbenic carbon centre resonates at very low field (331.5 ppm) in the expected region for metallaphosphirenes (*cf.* 266.3 ppm for **5**). The IR spectrum of **4** displays a single strong CO stretching absorption at 1954 cm^{-1} and its APCI mass spectrum exhibits a molecular ion peak.

The molecular structure ‡ of **4** is depicted in Fig. 1. The monomeric molecule is chiral and crystallises as a racemic mixture of enantiomerically pure crystals. The iridium centre is best described as having a heavily distorted trigonal bipyramidal geometry with the carbonyl ligand and P(1) in the axial positions and C(1), P(2) and P(3) in the equatorial sites. Although the P(1)–C(1) bond length is short [1.753(13) Å] for a single bonded interaction, it is similar to that in **5** [1.775(8) Å][6] and intracyclic P–C bond lengths in phosphirene complexes, *e.g.* 1.78 Å average in [PtCl$_2$(PEt$_3$){η^1-P(Ph)C(Ph)C(Ph)}].[9] Similarly, the Ir–C(1) distance at 1.918(14) Å is longer than Ir–CO interactions but close to the mean for all other crystallographically determined Ir–C double bonds, 1.918 Å.[10] This, combined with the fact that P(1) has a distorted pyramidal coordination environment with a stereochemically active lone pair, [C(2)C(1)P(1)C(6) torsion angle −77.9°], leaves little doubt that the formulation of **4** as a phosphidocarbene complex is correct.

We saw the possibility of treating **4** with 2e$^-$ donors (L) in order to convert it to 18e$^-$ terminal phosphavinyl complexes, [Ir(CO)(PPh$_3$)$_2$(L){η^1-C(Bu^t)=PCy}]. However, initial studies have shown that passing CO gas through a toluene solution of **4** lead rapidly and quantitatively to the displacement of one PPh$_3$

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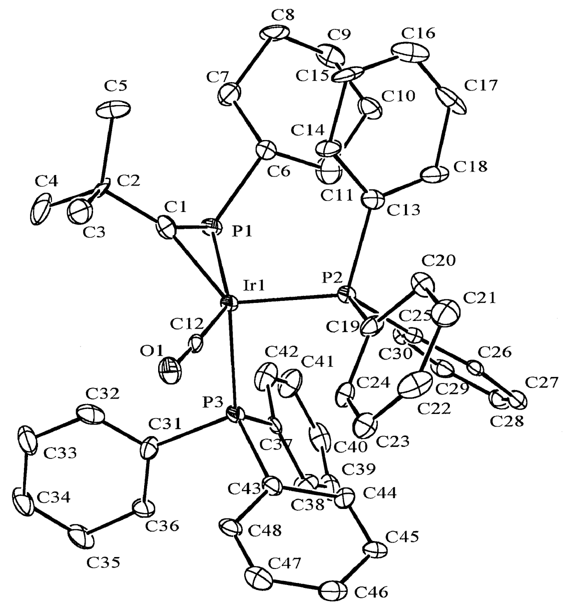

Fig. 1 Molecular structure of **4**. Selected bond lengths (Å) and angles (°): Ir(1)–C(12) 1.867(13), Ir(1)–C(1) 1.918(14), Ir(1)–P(2) 2.342(3), Ir(1)–P(3) 2.386(3), Ir(1)–P(1) 2.442(3), P(1)–C(1) 1.753(13), O(1)–C(12) 1.176(15); C(12)–Ir(1)–C(1) 104.4(5), C(12)–Ir(1)–P(2) 93.7(4), C(1)–Ir(1)–P(2) 127.5(4), C(12)–Ir(1)–P(3) 92.7(4), C(1)–Ir(1)–P(3) 128.2(4), P(2)–Ir(1)–P(3) 98.93(12), C(12)–Ir(1)–P(1) 149.1(4), C(1)–Ir(1)–P(1) 45.5(4), P(2)–Ir(1)–P(1) 110.33(11), P(3)–Ir(1)–P(1) 102.11(11), C(1)–P(1)–Ir(1) 51.3(4), P(1)–C(1)–Ir(1) 83.3(6).

ligand and formation of **6**. This was confirmed by the $^{31}P\{^{1}H\}$ NMR spectrum of this complex in which the signal corresponding to the phosphido centre (−152.3 ppm) has shifted only slightly down field from that in **4** but is now only coupled to one PPh_3 ligand ($^{2}J_{PP}$ = 79 Hz). In addition, the IR spectrum of **6** shows two strong CO stretching absorptions (1977, 1949 cm^{-1}).

Compound **6** is thermally stable in the solid state but in toluene or ethereal solutions decomposes over several hours to give many phosphorus containing products. We managed to isolate one of these, **7**, in very low yield (< 1%) but unfortunately were not able to obtain any data on this compound other than its X-ray crystal structure (Fig. 2). This is worthy of inclusion here as it demonstrates the ability of the phosphidocarbene ligand in **6** to undergo a facile intramolecular C–C bond forming reaction with one of its carbonyl ligands. This has given rise to a complex in which the oxo-η^3-phosphaallylic ligand adopts an *anti*-configuration, thus allowing its P-lone pair to intermolecularly donate to an Ir centre to give the observed 18e$^-$ dimeric structure for **7**. There is only one other crystallographically characterised example of an oxo-phosphaallylic complex, [Cp*Fe(CO){η^3-O=CC(H)P[C(H)(SiMe$_3$)$_2$]}] **8**, which was isolated as both its *syn*- and *anti*-isomers.[11] In **7**, the phosphaallylic ligand appears to be largely delocalised (as is the case in **8**) with both the P(1)–C(2) [1.800(8) Å] and C(1)–C(2) [1.433(11) Å] bond lengths lying between the norms for double and single bonded interactions.[10] The bond lengths from this ligand to Ir(1) confirm its η^3-mode of attachment and the C(1)–O(1) bond length [1.213(8) Å] is strongly suggestive of a localised double bond.

In conclusion, we have developed a facile synthetic route to the first example of an iridaphosphirene complex, **4**, which, based upon preliminary results, should prove to have a rich chemistry. We are currently looking at the reactions of **4** with a range or 2e$^-$ donors and other reagents, *e.g.* nitriles, isonitriles, carbenes, MeI *etc.* The results of our endeavours in this area will be reported in a forthcoming full paper.

Acknowledgements

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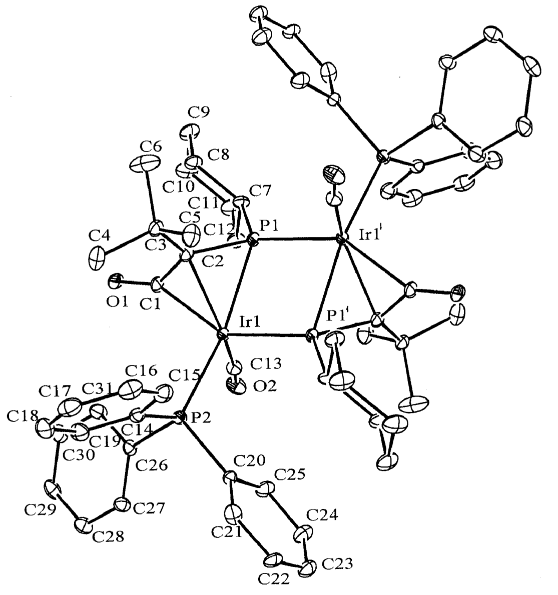

Fig. 2 Molecular structure of **7**. Selected bond lengths (Å) and angles (°): Ir(1)–C(13) 1.889(7), Ir(1)–C(1) 2.018(7), Ir(1)–C(2) 2.209(7), Ir(1)–P(2) 2.3481(19), Ir(1)–P(1) 2.3769(19), Ir(1)–P(1)′ 2.4550(17), P(1)–C(2) 1.800(8), O(1)–C(1) 1.213(8), C(1)–C(2) 1.433(11); C(1)–C(2)–P(1) 104.0(5), O(1)–C(1)–C(2) 139.7(8), C(2)–P(1)–C(7) 109.1(3), C(2)–P(1)–Ir(1)′ 122.1(2), Ir(1)–C(1)–O(1) 142.7(7), Ir(1)–P(1)–C(7) 116.9(2). Symmetry operation: ′ = −*x*, −*y* + 1, −*z*.

Notes and references

† Selected data for **4**: (yield 51%); mp 170–174 °C (dec.). ^{1}H NMR (400 MHz, C_6D_6, 300 K): δ 0.72–2.11 (m, 11H, Cy), 1.77 (s, 9H, Bu^t), 6.73–7.77 (m, 30H, ArH); ^{13}C NMR (101.6 MHz, C_6D_6, 300 K): δ 27.9 (m, C*C*H$_3$), 31.5 (m, CH), 33.6 (d, CH$_2$, $^{2}J_{PC}$ = 18 Hz), 34.2 (d, CH$_2$, $^{3}J_{PC}$ = 11 Hz), 36.4 (s, CH$_2$), 50.9 (m, *C*CH$_3$), 134.0 (d, *m*-ArC, $^{3}J_{PC}$ = 10 Hz), 134.5 (d, *o*-ArC, $^{2}J_{PP}$ = 13 Hz), 135.0 (s, *p*-ArC), 137.3 (m, *ipso*-ArC), 187.6 (dd, CO, $^{2}J_{PC}$ = 17 and 5 Hz), 331.5 (m, Ir=C); $^{31}P\{^{1}H\}$ NMR (121.7 MHz, C_6D_6) δ −157.2 (dd, Ir=CP, $^{2}J_{PP}$ = 22 and 66 Hz), 2.2 (dd, PPh$_3$, $^{2}J_{PP}$ = 22 and 66 Hz), 16.0 (v. tr., PPh$_3$, $^{2}J_{PP}$ = 22 and 22 Hz); MS APCI: *m*/*z* (%) 929 (MH$^+$, 15), 263 (PPh$_3$H$^+$, 100); IR (Nujol) ν/cm^{-1}: 1954(s) CO; Found: C, 46.67; H, 7.11; $C_{48}H_{50}OP_3Ir$ requires: C, 47.0; H, 7.10%.

For **6**: (yield 100%); mp 170–172 °C (dec.). ^{1}H NMR (400 MHz, C_6D_6, 300 K): δ 0.67–2.21 (m, 11H, Cy), 1.48 (s, 9H, Bu^t), 6.67–7.57 (m, 15H, ArH); $^{31}P\{^{1}H\}$ NMR (121.7 MHz, C_6D_6) δ −152.3 (d, Ir=CP, $^{2}J_{PP}$ = 79 Hz), 10.2 (d, PPh$_3$, $^{2}J_{PP}$ = 79 Hz); MS APCI: *m*/*z* (%) 666 (M − CO$^+$, 22), 262 (PPh$_3$$^+$, 100); IR (Nujol) ν/cm^{-1}: 1977(s), 1949(s).

‡ Crystal data for **4**: $C_{48}H_{50}OP_3Ir$, *M* = 927.99, orthorhombic, space group $P2_12_12_1$, *a* = 10.552(2), *b* = 12.359(3), *c* = 32.250(7) Å, *V* = 4205.8(15) Å^3, *Z* = 4, D_c = 1.466 g cm^{-3}, *F*(000) = 1872, μ(Mo-Kα) = 3.32 mm^{-1}, 150(2) K, 7325 unique reflections [*R*(int) = 0.0949], *R* (on *F*) = 0.0650, *wR* (on F^2) = 0.1401 ($I > 2\sigma I$).

For **7**: $C_{31}H_{35}O_2P_2Ir$, *M* = 693.73, monoclinic, space group $P2_1/n$, *a* = 11.381(2), *b* = 14.501(3), *c* = 16.922(3) Å, β = 94.83(3)°, *V* = 2782.8(10) Å^3, *Z* = 4, D_c = 1.656 g cm^{-3}, *F*(000) = 1376, μ(Mo-Kα) = 4.93 mm^{-1}, 150(2) K, 6327 unique reflections [*R*(int) = 0.0818], *R* (on *F*) = 0.0476, *wR* (on F^2) = 0.1033 ($I > 2\sigma I$). CCDC reference numbers 184725 and 184726. See http://www.rsc.org/suppdata/dt/b2/b204127h/ for crystallographic data in CIF or other electronic format.

1 D. E. Hibbs, C. Jones and A. F. Richards, *J. Chem. Soc., Dalton Trans.*, 1999, 3531.
2 C. Jones and A. F. Richards, *J. Chem. Soc., Dalton Trans.*, 2000, 3233.
3 C. Jones and A. F. Richards, *J. Organomet. Chem.*, 2001, **629**, 109.
4 C. Jones, J. A. Platts and A. F. Richards, *Chem. Commun.*, 2001, 663.
5 C. Jones, A. F. Richards, S. Fritzsche and E. Hey-Hawkins, *Organometallics*, 2002, **21**, 438.
6 N. H. T. Huy, J. Fischer and F. Mathey, *Organometallics*, 1988, **7**, 240.
7 L. Weber, G. Dembeck, H. G. Stammler, B. Neumann, M. Schmidtmann and A. Müller, *Organometallics*, 1998, **17**, 5254.
8 V. C. Gibson, T. P. Kee, S. T. Carter, R. D. Sanner and W. Clegg, *J. Organomet. Chem.*, 1991, **418**, 197.
9 S. S. Al-Juaid, D. Carmichael, P. B. Hitchcock, A. Marinetti, F. Mathey and J. F. Nixon, *J. Chem. Soc., Dalton Trans.*, 1991, 905.
10 Value determined from a search of the Cambridge Structural Database.
11 L. Weber, E. Lücke and R. Boese, *Chem. Ber.*, 1990, **123**, 23.