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Communications

Phosphapentadienyl–Iridium–Phosphine Chemistry.[1] Synthesis, Structure, and Spectroscopy of $(\mu\text{-}\eta^1\text{-phosphapentadienyl})_2Ir_2(PEt_3)_4$

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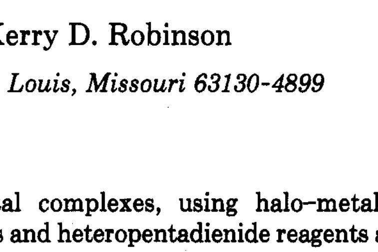
Summary: The first example of an anionic phosphapentadienide reagent, lithium phosphapentadienide, has been isolated and spectroscopically characterized. Reaction of this species with $(Cl)Ir(PEt_3)_3$ *yielded the phosphido-bridged iridium dimer* $(\mu\text{-}\eta^1\text{-phosphapentadienyl})_2Ir_2(PEt_3)_4$ *as trans and cis isomers (**1a** and **1b**, respectively). An X-ray crystal structure of **1a** has been obtained.*

During the past decade, the chemistry of metal complexes containing the acyclic pentadienyl group has been extensively investigated.[2] Through these studies, it has become evident that pentadienyl is a highly versatile ligand, capable of interacting with metal centers in a variety of hapticities and geometries.

In contrast to (pentadienyl)metal chemistry, relatively little effort has been directed toward synthesizing (heteropentadienyl)metal complexes, i.e., species in which one carbon atom of the pentadienyl chain has been replaced by a heteroatom. Like their all-carbon counterparts, heteropentadienyl ligands have the *potential* to bond to metals in a wide variety of modes. However, little is currently known about the relative energetics of these modes. In order to address this issue, we have begun a systematic exploration of the synthesis of (heteropentadienyl)metal complexes, using halo-metal-phosphine compounds and heteropentadienide reagents as our building blocks.[1] We now report the synthesis of the first anionic phosphapentadienide reagent, lithium phosphapentadienide,[3] and its reaction with $(Cl)Ir(PEt_3)_3$ to produce the novel phosphido-bridged iridium dimer $(\mu\text{-}\eta^1\text{-phosphapentadienyl})_2Ir_2(PEt_3)_4$ (1).

Treatment of butadienylphosphine, $H_2PCH{=}CHCH{=}CH_2$,[4] with *n*-butyllithium at −98 °C, followed by warming to room temperature, generated lithium phosphapentadienide as an orange, tetrahydrofuran-soluble solid.[5] The $^{13}C\{^1H\}$ NMR spectrum of this species showed four downfield signals at δ 154.0 (d, $J_{C\text{-}P}$ = 40 Hz, C4), 142.0 (s, C2), 122.0 (s, C3), and 95.6 (s, C1). Similarly, downfield signals were observed in the ^1H NMR spectrum at δ 6.90 (m, H4), 6.09 (m, H2), 5.89 (m, H3), 4.12 (d, $J_{H\text{-}H2}$ = 16.1 Hz, $H1_{anti}$), and 3.87 (d, $J_{H\text{-}H2}$ = 9.6 Hz, $H1_{syn}$). The phosphido proton (H5) resonated at δ 1.88 and was a doublet of doublets due to a large phosphorus coupling ($J_{H\text{-}P}$ = 160 Hz) and a much smaller proton coupling ($J_{H\text{-}H4}$ = 12.5 Hz). The phosphorus center gave rise to a singlet at δ −107.2 in the $^{31}P\{^1H\}$ NMR spectrum. In the absence of ^1H decoupling, this signal split into a doublet of doublets



[⊗] Abstract published in *Advance ACS Abstracts,* December 15, 1993.

(1) Pentadienyl-Metal-Phosphine Chemistry. 26. Previous papers in this series include: (a) Bleeke, J. R.; Haile, T.; New, P. R.; Chiang, M. Y. *Organometallics* **1993**, *12*, 517. (b) Bleeke, J. R.; Ortwerth, M. F.; Chiang, M. Y. *Organometallics* **1992**, *11*, 2740.

(2) For leading reviews, see: (a) Ernst, R. D. *Chem. Rev.* **1988**, *88*, 1251. (b) Yasuda, H.; Nakamura, A. *J. Organomet. Chem.* **1985**, *285*, 15. (c) Powell, P. *Adv. Organomet. Chem.* **1986**, *26*, 125.

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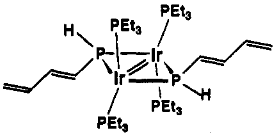
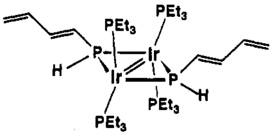
of doublets with couplings of 160, 36, and 5 Hz due to H5, H4, and H3, respectively.

Treatment of (Cl)Ir(PEt$_3$)$_3$ with lithium phosphapentadienide in tetrahydrofuran at 0 °C, followed by warming to ~50 °C for 4 h, led to the production of a red toluene-soluble solid.[6] The ^{31}P{^{1}H} NMR spectrum of this product[7] showed the presence of two solution-phase isomers in an approximate 1.4:1 ratio. The major isomer exhibited a quintet (J = 19 Hz) at δ 68.0 (intensity 1) and a triplet (J = 19 Hz) at δ -4.1 (intensity 2), while the minor isomer gave rise to three equal-intensity multiplets at δ 66.4, 1.0, and -10.0. From the multiplicities of the major isomer peaks, we reasoned that this species was a symmetric iridium dimer containing two bridging phosphido ligands and four equivalent terminal PEt$_3$ ligands. A likely structure was "trans" dimer **1a**. The minor isomer was then postulated to be the less symmetric "cis" dimer, **1b**. Consistent with these proposed structures were the downfield ^{31}P NMR chemical shifts of the bridging phosphido ligands (δ 68.0 in **1a** and δ 66.4 in **1b**), which argued for a strong metal–metal interaction,[8] and the small P–P coupling constants (19 Hz in **1a**), which implied a tetrahedral geometry about each iridium center.[9] The ^{13}C and ^{1}H NMR signals of the phosphapentadienyl ligands in **1a** and **1b** were very similar to those of the anionic phosphapentadienide reagent. The only major difference was the position of the phosphido hydrogen (H5), which shifted dramatically downfield (to δ 8.83 in **1a** and δ 8.58 in **1b**) and in each case appeared as a broad doublet of doublets with coupling constants $^1J_{\mathrm{H-P_{phosphido}}} \approx$ 200 Hz and $^3J_{\mathrm{H-P_{phosphido}}} \approx$ 100 Hz.



1a (*trans* isomer)



1b (*cis* isomer)

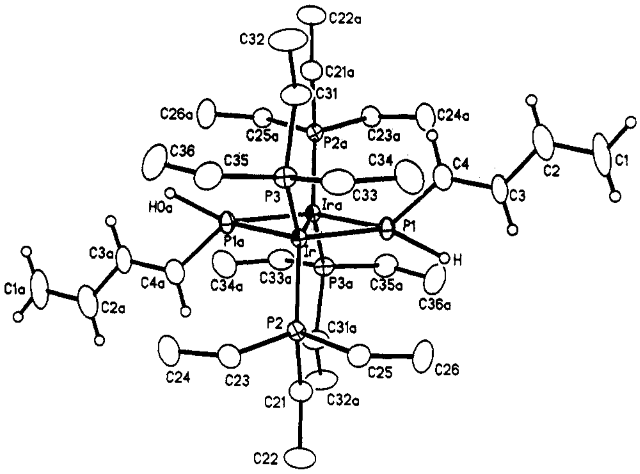


Figure 1. ORTEP drawing of (μ-η^1-phosphapentadienyl)$_2$Ir$_2$(PEt$_3$)$_4$ (**1a**). Selected bond distances (Å): Ir–Ira, 2.576(1); Ir–P1, 2.291(1); Ir–P1a, 2.292(1); Ir–P2, 2.249(2); Ir–P3, 2.259(2); C1–C2, 1.326(10); C2–C3, 1.465(10); C3–C4, 1.347(8); P1–C4, 1.787(6). Selected bond angles (deg): P1–Ir–P1a, 111.6(1); P1–Ir–P2, 108.4(1); P1–Ir–P3, 114.7(1); P1a–Ir–P2, 115.5(1); P1a–Ir–P3, 109.5(1); P2–Ir–P3, 96.5(1); Ir–P1–Ira, 68.4(1); C1–C2–C3, 123.1(10); C2–C3–C4, 123.5(8); C3–C4–P1, 127.6(7); C4–P1–Ir, 123.9(2); C4–P1–Ira, 128.1(3).

Crystals of **1a** were grown from a saturated toluene solution at -40 °C, and its solid-state structure was confirmed by a single-crystal X-ray diffraction study[10] (see ORTEP drawing, Figure 1). The complex resided on a crystallographically imposed inversion center, making the two Ir(PEt$_3$)$_2$ fragments and the two bridging phosphido ligands crystallographically equivalent. As predicted, the coordination geometry about iridium was approximately tetrahedral. The six P–Ir–P angles ranged from 96.5 to 115.5°, averaging 109.4°. The Ir–Ir distance was 2.576(1)

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(3) Recently, the first anionic phosphaallyl reagent was reported: Niecke, E.; Nieger, M.; Wenderoth, P. *J. Am. Chem. Soc.* **1993**, *115*, 6989.

(4) Cabioch, J. L.; Denis, J. M. *J. Organomet. Chem.* **1989**, *377*, 227.

(5) Synthesis of lithium phosphapentadienide: Under nitrogen, butadienylphosphine (2.0 g, 0.023 mol) was mixed with 50 mL of diethyl ether and 10 mL of tetrahydrofuran and cooled to -98 °C in a methanol/N$_2$(l) bath. *n*-Butyllithium (14.4 mL of a 1.6 M solution in hexanes, 0.023 mol) was diluted with ~10 mL of diethyl ether and added dropwise over a period of 30 min. A yellow/orange color formed immediately in the solution. After it was slowly warmed to room temperature, the solution was stirred for 8 h and filtered through Celite. The solvent was then removed under vacuum, yielding lithium phosphapentadienide as a gummy orange solid (crude yield 2.0 g, 95%). A free-flowing orange powder was obtained by washing the crude product with three 200-mL aliquots of diethyl ether. This powder was extremely air-sensitive, burning upon exposure to the atmosphere.

(6) Synthesis of 1: Under nitrogen, triethylphosphine (0.16 g, 1.34 mmol) was added dropwise to a stirred solution of [(cyclooctene)$_2$Ir(Cl)]$_2$ (0.20 g, 0.22 mmol) in 10 mL of tetrahydrofuran (THF). The volatiles were removed under vacuum, and the resulting residue was redissolved in 50 mL of THF and cooled to 0 °C. Lithium phosphapentadienide (0.041 g, 0.45 mmol) in 20 mL of THF was added dropwise, causing the solution to turn deep red. After the mixture was stirred overnight, it was heated gently (at ~50 °C) for 4 h. The volatiles were then removed under vacuum, and the residue was extracted with toluene. The resulting red solution was filtered and evaporated to dryness, yielding 0.15 g (67%) of 1 as a 1.4:1 ratio of *trans* to *cis* isomers (**1a**:**1b**). When this product was redissolved in a minimal quantity of toluene and cooled to -40 °C, **1a** crystallized as red plates. Anal. Calcd for $C_{32}H_{72}Ir_2P_6$: C, 37.41; H, 7.08. Found: C, 36.93; H, 6.64.

(7) Spectroscopic data for 1 are as follows (carbon atoms in the chain are numbered by starting from the end opposite phosphorus). *trans* isomer, **1a**: ^{31}P{^{1}H} NMR (C_6D_6, 22 °C, 121 MHz, referenced to external H_3PO_4) δ 68.0 (quintet, $J_{\mathrm{P-P}}$ = 19.0 Hz, 1, phosphido P), -4.1 (triplet, $J_{\mathrm{P-P}}$ = 19.0 Hz, 2, PEt$_3$'s); ^{13}C{^{1}H} NMR (C_6D_6, 22 °C, 75 MHz) δ 145.5 (C4), 138.7 (C2), 129.5 (C3), 115.2 (C1), 24.3 (PEt$_3$ CH$_2$'s), 9.0 (PEt$_3$ CH$_3$'s); ^{1}H NMR (C_6D_6, 22 °C, 300 MHz) δ 8.83 (dd, $^1J_{\mathrm{H-P}}$ = 200 Hz, $^3J_{\mathrm{H-P}}$ = 100 Hz, 1, H5), 6.82 (br m, 1, H3), 6.70 (br m, 1, H4), 6.55 (br m, 1, H2), 5.21 (d, $J_{\mathrm{H-H2}}$ = 16.5 Hz, 1, H1$_{\mathrm{anti}}$), 4.93 (d, $J_{\mathrm{H-H2}}$ = 9.9 Hz, 1, H1$_{\mathrm{syn}}$), 1.35 (br m, 12, PEt$_3$ CH$_2$'s), 0.98 (br m, 18, PEt$_3$ CH$_3$'s); IR (KBr pellet) 2956 (vs), 2926 (vs), 2904 (s), 2872 (s), 2194 (s), 1609 (s), 1559 (m), 1457 (s), 1436 (m), 1430 (m), 1419 (m), 1248 (m), 1141 (s), 1027 (vs), 997 (s), 955 (m), 886 (s), 755 (vs), 709 (vs), 621 (s) cm^{-1}. *cis* isomer, **1b** (peak positions obtained from a mixture of **1a** and **1b**): ^{31}P{^{1}H} NMR (C_6D_6, 22 °C, 121 MHz, referenced to external H_3PO_4) δ 66.4 (br m, 1, phosphido P), 1.0 (br m, 1, PEt$_3$), -10.0 (br m, 1, PEt$_3$); ^{13}C{^{1}H} NMR (C_6D_6, 22 °C, 75 MHz) δ 146.7 (C4), 138.7 (C2), 129.8 (C3), 115.0 (C1), 25.1 (PEt$_3$ CH$_2$'s), 23.2 (PEt$_3$ CH$_2$'s), 9.3 (PEt$_3$ CH$_3$'s), 8.8 (PEt$_3$ CH$_3$'s); ^{1}H NMR (C_6D_6, 22 °C, 300 MHz) δ 8.58 (dd, $^1J_{\mathrm{H-P}}$ = 200 Hz, $^3J_{\mathrm{H-P}}$ = 100 Hz, 1, H5), 7.14–6.48 (m's, 3, H4, H3, H2), 5.17 (d, $J_{\mathrm{H-H2}}$ = 17.0 Hz, 1, H1$_{\mathrm{anti}}$), 4.96 (d, $J_{\mathrm{H-H2}}$ = 9.0 Hz, 1, H1$_{\mathrm{syn}}$), 1.35 (br m, 12, PEt$_3$ CH$_2$'s), 0.98 (br m, 18, PEt$_3$ CH$_3$'s).

(8) Downfield ^{31}P NMR shifts of phosphido ligands bridging metal–metal bonds are common. See, for example: (a) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229. (b) Carty, A. J. *Adv. Chem. Ser.* **1982**, *No. 196*, 163.

(9) Small P–P coupling constants are characteristic of phosphido-bridged dimers containing terminal phosphine ligands and tetrahedral metals. See, for example: (a) Kreter, P. E.; Meek, D. W. *Inorg. Chem.* **1983**, *22*, 319. (b) Jones, R. A.; Norman, N. C.; Seeberger, M. H.; Atwood, J. L.; Hunter, W. E. *Organometallics* **1983**, *2*, 1629. (c) Burkhardt, E. W.; Mercer, W. C.; Geoffroy, G. L. *Inorg. Chem.* **1984**, *23*, 1779.

(10) Crystal data for **1a**: red plate, 0.08 × 0.56 × 0.22 mm; triclinic, space group $P\bar{1}$, a = 10.031(2) Å, b = 10.795(2) Å, c = 11.965(2) Å, α = 67.92(2)°, β = 84.70(2)°, γ = 65.81(2)°, V = 1092.3(3) Å^3, Z = 1, d_{calcd} = 1.561 g/cm^3, μ = 63.23 cm^{-1}; Siemens R3m/V diffractometer, graphite-monochromated Mo Kα radiation, 22 °C, θ–2θ scanning technique; 3871 unique reflections with 3.0° < 2θ < 50.0° collected, 3423 reflections with $F > 6.0\sigma(F)$ used in refinement; semiempirical absorption correction (ψ scans); R = 0.0240, R_w = 0.0310, GOF = 1.04, data-to-parameter ratio 18.4:1. The phosphido proton (H5) was located and refined isotropically.

Å, consistent with the presence of a double bond,[11] as required for each metal to achieve an 18e$^-$ count. The phosphapentadienyl ligand was essentially W-shaped with torsional angles of 179.2 and −175.5° for C1–C2–C3–C4 and C2–C3–C4–P1, respectively. The carbon–carbon bond lengths showed the expected pattern of alternation, while the angles within the ligand were all expanded slightly from their theoretical value of 120° (see caption to Figure 1).

While phosphido-bridged iridium dimers of this general structure are known,[9a,11] all contain dialkyl- or diarylphosphido groups. To our knowledge, this is the first example of a *primary* phosphido–iridium dimer and the first iridium system to exhibit *cis*/*trans* isomers. Perhaps the closest known analogue of **1** is (μ-P(H)(*t*-Bu))$_2$Rh$_2$(PMe$_3$)$_4$, reported by Jones et al.[9b] However, this complex possesses two substituents on the bridging phosphido group which are very different in size and, as a result, it exists only as the less sterically encumbered *trans* isomer.

When pure (crystalline) *trans* isomer **1a** was dissolved in benzene, it slowly isomerized back to the equilibrium mixture of **1a** and **1b** (1.4:1). Several possible mechanisms can be envisaged for the isomerization. Perhaps the simplest is dissociation of one iridium–phosphido bond, inversion at the resulting terminal phosphido phosphorus center, and reformation of the iridium–phosphido bond. While phosphorus inversion barriers are generally quite high, recent work by Gladysz et al.[12] has shown that $\Delta G^{\ddagger}$ for phosphorus inversion in terminal primary phosphido ligands is remarkably low—in the range of 11–15 kcal/mol. A second possible mechanism involves reversible dissociation of the dimers into monomeric (phosphapentadienyl)Ir(PEt$_3$)$_2$ complexes.[13]

In order to distinguish between these two mechanistic alternatives, we synthesized the diethylphenylphosphine analogue of **1**, (μ-η^1-phosphapentadienyl)$_2$Ir$_2$(PEt$_2$Ph)$_4$ (**2**).[14] Like **1**, compound **2** crystallized from toluene as the *trans* isomer but slowly converted in benzene solution to a 1.4:1 equilibrium mixture of *trans* (**2a**) and *cis* (**2b**) isomers. When crystalline samples of pure *trans* isomers **1a** and **2a** were dissolved together in benzene at room temperature, we observed the gradual formation of the *cis* isomers **1b** and **2b**.[15] However, no additional peaks due to the "mixed" dimer (PEt$_3$)$_2$Ir(μ-η^1-phosphapentadienyl)$_2$Ir(PEt$_2$Ph)$_2$ were detected in either the phosphide or phosphine region of the ^{31}P NMR spectrum. This result rules out reversible dissociation of dimers into monomeric complexes *under these rather mild conditions* and supports the intramolecular process involving inversion at the phosphido phosphorus center.

The reaction chemistry of compounds **1** and **2** is now under investigation. One particularly intriguing possibility is that these species might serve as building blocks for the construction of novel one-dimensional polymers containing doubly bonded diiridium subunits.[16] Various strategies for coupling the dienyl moieties of the μ-η^1-phosphapentadienyl ligands are currently being probed.

Acknowledgment. We thank the National Science Foundation (Grants CHE-9003159 and CHE-9303516) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. A loan of IrCl$_3$·3H$_2$O from Johnson-Matthey Alfa/Aesar is gratefully acknowledged. Washington University's X-ray Crystallography Facility was funded by the National Science Foundation's Chemical Instrumentation Program (Grant CHE-8811456). The High Resolution NMR Service Facility was funded in part by National Institutes of Health Biomedical Support Instrument Grant 1 S10 RR02004 and by a gift from Monsanto Co.

Supplementary Material Available: Structure determination summary table and listings of final atomic coordinates, thermal parameters, bond lengths, and bond angles for compound **1a** (8 pages). Ordering information is given on any current masthead page.

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[11] (a) Mason, R.; Sotofte, I.; Robinson, S. D.; Uttley, M. R. *J. Organomet. Chem.* **1972**, *46*, C61. (b) Bellon, P. L.; Benedicenti, C.; Caglio, G.; Manassero, M. *J. Chem. Soc., Chem. Commun.* **1973**, 946. (c) Arif, A. M.; Heaton, D. E.; Jones, R. A.; Kidd, K. B.; Wright, T. C.; Whittlesey, B. R.; Atwood, J. L.; Hunter, W. E.; Zhang, H. *Inorg. Chem.* **1987**, *26*, 4065.

[12] Zwick, B. D.; Dewey, M. A.; Knight, D. A.; Buhro, W. E.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1992**, *11*, 2673.

[13] An analogous mechanism has been postulated for the isomerization of a related rhodium dimer containing μ-PMePh ligands.[9c]

[14] Synthesis and selected spectroscopic data for **2**: A synthetic procedure strictly analogous to that described above for **1** was employed. ^{31}P{^{1}H} NMR (C$_6$D$_6$, 22 °C, 121 MHz, referenced to external H$_3$PO$_4$): *trans* isomer, **2a**, δ 71.1 (quintet, J_{P-P} = 18.5 Hz, 1, phosphido P), −2.1 (t, J_{P-P} = 18.5 Hz, 2, PEt$_2$Ph's); *cis* isomer, **2b**, δ 71.1 (br m, 1, phosphido P), 5.3 (br m, 1, PEt$_2$Ph), −10.1 (br m, 1, PEt$_2$Ph).

[15] The reaction was carried out in the dark to eliminate the slow photoassisted decomposition of **1** and **2**.

[16] Cayton, R. H.; Chisholm, M. H.; Huffman, J. C.; Lobkovsky, E. B. *J. Am. Chem. Soc.* **1991**, *113*, 8709 and references cited therein.