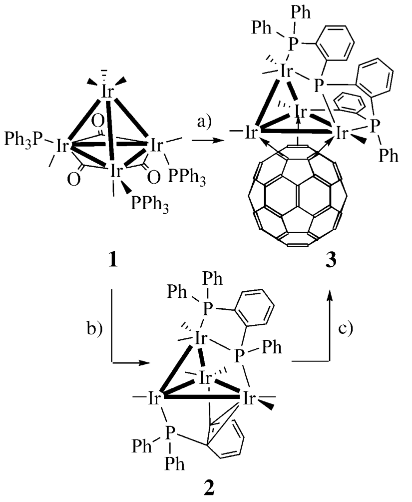
Phosphane Ligands

Novel [60]Fullerene-Assisted *ortho*-Phosphanation on a Tetrairidium Butterfly Framework[**]

*Bo Keun Park, M. Arzu Miah, Gaehang Lee, Youn-Jaung Cho, Kwangyeol Lee, Sangwoo Park, Moon-Gun Choi, and Joon T. Park**

The extensive use of [60]fullerene, the most abundant member of the fullerene family, as a ligand in organometallic chemistry has been attributed to its pivotal role in material science owing to its unique electronic, optical, and magnetic properties.[1] In particular, the interaction of a carbon cluster such as C_{60} with metal clusters has been a topic of great interest in exohedral metallofullerene chemistry,[2] because C_{60}–metal cluster complexes have a direct analogy to carbon nanotubes decorated with metal nanoparticles.[3] Furthermore, they exhibit very strong electronic communication between C_{60} and metal-cluster centers that can be fine-tuned by ligands attached to the metal atoms.[2a] As part of our studies on the chemistry of C_{60}–metal cluster complexes, we examined the reaction between the phosphane-substituted iridium carbonyl cluster $[\mathrm{Ir_4(CO)_9(PPh_3)_3}]$ (**1**)[4] and C_{60}. We demonstrated a new behavior of C_{60} as a noninnocent ligand, stemming from its multifunctionality, for the chemical transformation of ligands on the cluster surface. Here we report a novel C_{60}-induced formation of a P-(C)$_n$-P-(C)$_n$-P moiety by a series of *ortho*-phosphanation and *ortho*-metalation reactions of phosphanes on a tetrairidium butterfly framework (Scheme 1).



Scheme 1. a) 2 equiv C_{60}, ClC_6H_5, 132 °C, 3 h, 36 %; b) ClC_6H_5, 132 °C, 40 min, 64 %; c) 2 equiv C_{60}, ClC_6H_5, 132 °C, 3 h, 41 %.

Heating a mixture of **1** and 2 equiv of C_{60} in refluxing chlorobenzene (CB) for 2 h afforded $[\mathrm{Ir_4(CO)_6}\{\mu_3\text{-PPh}_2(o\text{-C}_6\text{H}_4)\text{P}(o\text{-C}_6\text{H}_4)\text{PPh}(\eta^1\text{-}o\text{-C}_6\text{H}_4)\}(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-C}_{60})]$ (**3**) in moderate yield (36 %). Thermolysis of **1** in refluxing CB gave $[\mathrm{Ir_4(CO)_8}\{\mu\text{-PPh}_2(o\text{-C}_6\text{H}_4)\text{PPh}\}\{\mu_3\text{-PPh}_2(\eta^1{:}\eta^2\text{-}o\text{-C}_6\text{H}_4)\}]$ (**2**) in 64 % yield. Reaction of **2** with C_{60} in refluxing CB produced **3** in 41 % yield, that is, **2** is indeed the reaction intermediate for the final product **3** (see Scheme 1 and Experimental Section). The formulas of **2** and **3** were established by microanalytical data and molecular-ion isotope multiplets at *m*/*z* 1624 for **2** and 2210 for **3** in the positive-ion FAB mass spectra.

The molecular structures of **2** and **3** are shown in Figures 1 and 2, respectively. Both complexes exhibit a butterfly geometry of four iridium atoms, in which the two wings are nearly perpendicular to each other, as was observed in previously reported wingtip-bridged Ir_4 butterfly complexes.[5] The P1 atom bearing two phenyl groups in **2** is coordinated to the Ir4 center, and the two wingtip Ir atoms are almost symmetrically bridged by the P2 atom. An *o*-phenylene group bridges the P1 and P2 atoms in the bidentate diphosphane moiety $\mathrm{Ph_2P}(o\text{-C}_6\text{H}_4)\mathrm{PPh}$, which in turn forms a five-membered metallacyclic P1-C301-C306-P2-Ir4 moiety on the cluster. Another interesting structural feature of **2** is the presence of a $\mu_3\text{-PPh}_2(\eta^1{:}\eta^2\text{-}o\text{-C}_6\text{H}_4)$ ligand (a five-electron donor), which is coordinated through P3 to the Ir3 atom by an Ir−C(phenylene) σ bond to the Ir2 center, and by an η^2 interaction of the $o\text{-C}_6\text{H}_4$ ring to the Ir1 atom. A similar bonding mode was previously observed in [(μ-H)-

---

[*] B. K. Park, Dr. M. A. Miah, G. Lee, Y.-J. Cho, Prof. J. T. Park
National Research Laboratory,
Department of Chemistry and School of Molecular Science (BK 21)
Korea Advanced Institute of Science and Technology
Daejeon, 305-701 (Korea)
Fax: (+82) 42-869-5826
E-mail: joontpark@kaist.ac.kr
Prof. K. Lee
Department of Chemistry, Korea University
Seoul, 136-701 (Korea)
S. Park, Prof. M.-G. Choi
Department of Chemistry and Molecular Structure Laboratory
Yonsei University, Seoul, 120-749 (Korea)

[**] This research was supported by the National Research Laboratory (NRL) Program of the Korean Ministry of Science & Technology (MOST), the Korea Science & Engineering Foundation (KOSEF, Project No. 1999-1-122-001-5) for J.T.P., and a Korea University Grant for K.L.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

© 2004 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim DOI: 10.1002/anie.200353290

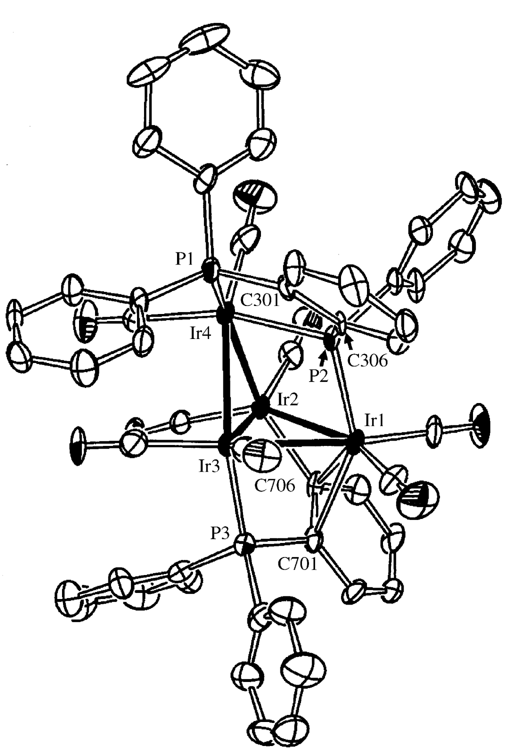


Figure 1. Molecular structure with atomic labeling scheme for **2**. Selected bond lengths [Å] and angles [°]: Ir1–Ir2 2.6953(6), Ir1–Ir3 2.7170(7), Ir2–Ir3 2.6689(6), Ir2–Ir4 2.7409(6), Ir3–Ir4 2.8054(6), Ir1–C701 2.55(1), Ir1–C706 2.41(1), Ir2–C706 2.08(1); Ir1-Ir2-Ir4 88.20(2), Ir1-Ir3-Ir4 86.46(2).

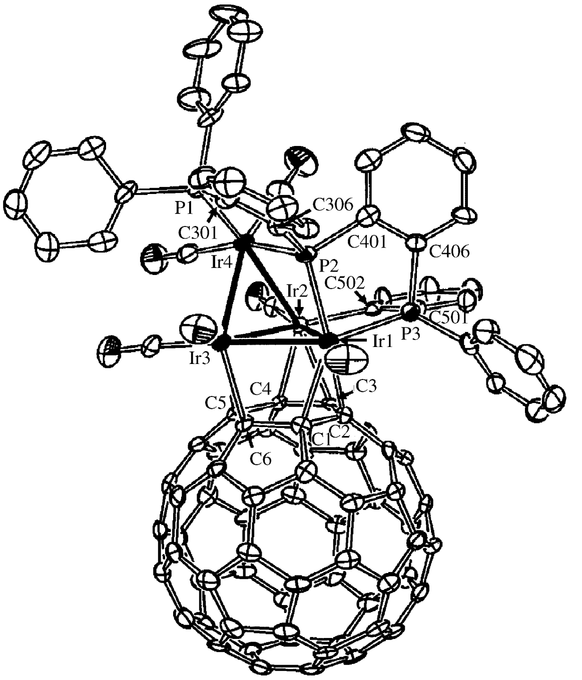
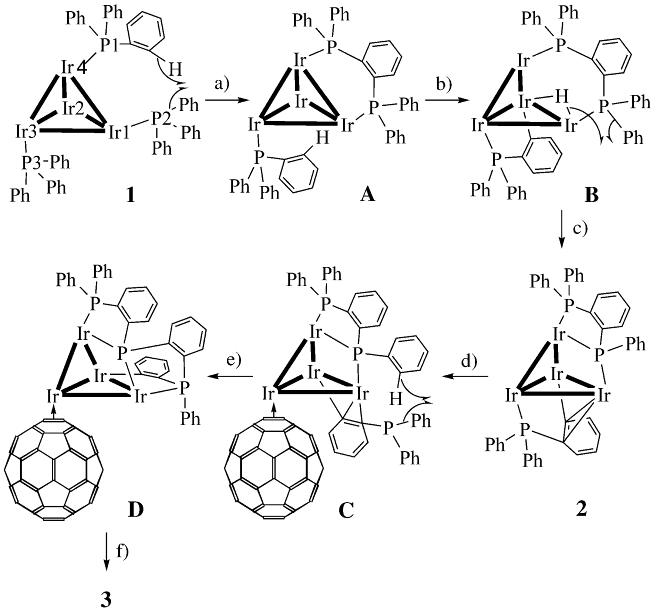


Figure 2. Molecular structure with atomic labeling scheme for **3**. Selected bond lengths [Å] and angles [°]: Ir1–Ir2 2.7598(8), Ir1–Ir3 2.7827(8), Ir2–Ir3 2.8059(7), Ir2–Ir4 2.7401(9), Ir3–Ir4 2.8094(7), Ir2–C502 2.089(8); Ir1-Ir2-Ir4 85.02(1), Ir1-Ir3-Ir4 83.30(2).

$Os_3(CO)_8\{\mu_3\text{-}PPhMe(\eta^1{:}\eta^2\text{-}C_6H_4)\}]$[6] and $[(\mu\text{-}H)Ru_3(CO)_8\{\mu_3\text{-}PPh(\eta^1{:}\eta^2\text{-}C_6H_4)(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_4PPh_2)\}]$.[7] In **3**, the P1 atom bearing two phenyl groups is coordinated to the Ir4 atom, and the P2 atom bridges the two wingtip Ir1 and Ir4 atoms similarly to **2**. The phenyl group on the P2 atom has been *ortho*-phosphanated by the P3 atom, and a phenyl group on the P3 center underwent *ortho*-metalation to form five-membered Ir1-P2-C401-C406-P3 and Ir1-Ir2-C502-C501-P3 metallacycles, respectively. Overall, the three PPh_3 ligands in **1** are converted to a triphosphane ligand $Ph_2P(o\text{-}C_6H_4)P(o\text{-}C_6H_4)PPh(\eta^1\text{-}o\text{-}C_6H_4)$ in **3**. The C–C bonds in the $\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60}$ ligand alternate in length, with an average long distance of 1.49(1) and an average short distance of 1.43(1) Å. This face-capping C_{60} bonding mode is well documented for a variety of cluster frameworks.[2a]

A plausible reaction mechanism for **1**→**2**→**3** is proposed in Scheme 2. The first step is an *ortho*-phosphanation in **1** to form intermediate **A**. *ortho*-Metalation of a phenyl group on the P3 atom in **A** results in rupture of the Ir1–Ir4 bond to form the hydrido butterfly intermediate **B** (62 valence electrons). Binuclear reductive elimination of C_6H_6 and the loss of a carbonyl ligand in **B** induces coordination of the P2 atom to the Ir4 center and π coordination of the *ortho*-metalated phenyl ring to form an $\eta^1{:}\eta^2\text{-}o\text{-}C_6H_4$ moiety in **2**. The next step is cleavage of the Ir3–P3 bond and subsequent coordination of $\eta^2\text{-}C_{60}$ to produce intermediate **C**. Another *ortho*-phosphanation reaction in **C** takes place to form a triphosphane moiety, and the π interaction in the $\eta^1{:}\eta^2\text{-}o\text{-}C_6H_4$ ligand is replaced by coordination of the P3 atom to the Ir1 center to give intermediate **D**. The final product **3** is produced by the loss of two carbonyl ligands and face-capping of the C_{60} ligand in the $\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2$ fashion.



Scheme 2. a) $-C_6H_6$; b) *ortho*-metalation of a phenyl group on P3; c) $-C_6H_6$, $-CO$; d) $+C_{60}$; e) $-C_6H_6$; f) $-2\,CO$.

© 2004 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

In the transformation **1**→**2**→**3**, three PPh_3 ligands are converted to the diphosphane μ_2-$Ph_2P(o$-$C_6H_4)PPh$ and in turn to the triphosphane μ_3-$PPh_2(o$-$C_6H_4)P(o$-$C_6H_4)PPh(\eta^1$-o-$C_6H_4)$ on the Ir_4 cluster framework by successive *ortho*-phosphanation and *ortho*-metalation processes, as described in Scheme 2. Synthesis of phosphane ligands with P-(C)$_n$-P and P-(C)$_n$-P-(C)$_n$-P donor sequences is of special interest, because of their ability to bridge metal–metal bonds and thus to stabilize oligometallic or metal cluster complexes. Such phosphane ligands have usually been prepared by tedious multistep organic synthesis.[8] We have now demonstrated that facile *ortho*-phosphanation and *ortho*-metalation can take place on an Ir_4 framework and, more importantly, the multifunctional C_{60} ligand can assist the *ortho*-phosphanation step, as in the conversion of **2** to **3**. To the best of our knowledge, this is the first example not only of facile *ortho*-phosphanation on transition metals but also of the C_{60} molecule acting as a noninnocent ligand that assists unusual phosphane-transformation reactions.

We are currently investigating the detailed mechanistic pathways of **1**→**2**→**3** and trying to develop facile synthetic methods for multifunctional phosphanes from coupling reactions of phosphanes on Ir_4 carbonyl clusters in the presence of C_{60} and dihydrogen.

Experimental Section

Details on the synthesis as well as a full spectroscopic characterization of **2** and **3** and the conversion of **2** to **3** are given in the Supporting Information. X-ray structural data were collected on a CCD diffractometer with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) using ω scans. CCDC-221530 (**2**) and CCDC-221531 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

2: Elemental analysis (%) calcd for $C_{50}H_{33}Ir_4O_8P_3$: C 36.99, H 2.05; found: C 36.76, H 2.19; IR (C_6H_{12}): $\tilde{\nu}$(CO) = 2062 (w), 2049 (s), 2029 (vs), 2011 (vs), 1993 (vs), 1956 (m), 1946 cm^{-1} (m); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): $\delta = 8.44$ (dd, 1H, $J_{PH} = 8.0$ Hz, $J_{PH} = 2.5$ Hz), 7.89 (m, 1H), 7.63 (m, 4H), 7.46–6.88 (m, 24H), 6.62 (m, 2H), 6.51 ppm (t, 1H, $J_{PH} = 7.6$ Hz) (all $C_6H_5 + C_6H_4$); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): $\delta = 186.8$ (s, 1CO), 185.7 (s, 1CO), 179.6 (s, 1CO), 176.4 (s, 1CO), 166.4(s, 1CO), 165.7 (s, 1CO), 165.5 (d, 1CO, $^2J_{CP} = 3.5$ Hz), 163.7 (d, 1CO, $^2J_{CP} = 4$ Hz), 153.2–124.3 (42C, $C_6H_5 + C_6H_4$); ^{31}P{H} NMR (122 MHz, $CDCl_3$, 298 K): $\delta = 24.2$ (d, 1P, $^3J_{PP} = 22.1$ Hz), 16.4 (s, 1P), −42.9 (d, 1P, $^3J_{PP} = 22.1$ Hz); MS (FAB$^+$): m/z: 1624 [M^+].

X-ray crystal data for **2**: Orange crystals were obtained by slow diffusion of methanol into a solution of **2** in CH_2Cl_2 at room temperature. The crystal used for data collection contained no solvent molecules ($C_{50}H_{33}P_3O_8Ir_4$, $M_r = 1623.47$): triclinic, space group $P\bar{1}$, $Z = 2$, $\rho_{calcd} = 2.256$ g cm^{-3}, $a = 11.087(1)$, $b = 11.472(1)$, $c = 21.576(2)$ Å, $\alpha = 91.925(2)$, $\beta = 101.719(2)$, $\gamma = 116.070(1)°$, $V = 2390.1(4)$ Å^3. The structure was solved by direct methods and refined by full-matrix least-squares analysis to give $R = 0.0576$ and $R_w = 0.1476$ (based on F^2) for 586 parameters and 10924 unique reflections with $I > 2\sigma(I)$ and $1.95 < \theta < 28.02°$. Data was collected at $T = 293(2)$ K.

3: Elemental analysis (%) calcd for $C_{102}H_{27}Ir_4O_6P_3$: C 55.43, H 1.23; found: C 55.64, H 1.42. IR (CH_2Cl_2): $\tilde{\nu}$(CO) = 2045 (vs), 2016 (vs), 1998 (s), 1985 (sh), 1970 cm^{-1} (m); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): $\delta = 7.14$–8.07 (m, 24H); 6.78–6.93 ppm (m, 3H) (all $C_6H_5 + C_6H_4$); ^{13}C NMR (100 MHz, $C_6D_4Cl_2$, 298 K): $\delta = 188.4$ (d, 1CO, $J_{PC} = 2.5$ Hz), 187.3 (d, 1CO, $J_{PC} = 3.2$ Hz), 179.9 (s, 1CO), 173.3 (t, 1CO, $J_{PC} = 3.9$ Hz), 172.4 (d, 1CO, $J_{PC} = 12.2$ Hz), 161.2 (dd, 1CO, $J_{PC} = 51.2$ Hz, $J_{PC} = 5.5$ Hz), 158.9–143.6 (54C, C_{60} sp^2 region), 79.1 (d, 1C, $J_{PC} = 6.3$ Hz, C_{60} sp^3 π-bonded C) 68.0 (t, 1C, $J_{PC} = 4.9$ Hz, C_{60} sp^3 π-bonded C), 64.1 (d, 1C, $J_{PC} = 2.4$ Hz, C_{60} sp^3 π-bonded C), 62.7 (s, 1C, C_{60} sp^3 π-bonded C), 61.2 (d, 1C, $J_{PC} = 4.5$ Hz, C_{60} sp^3 π-bonded C), 60.6 ppm (dd, 1C, $J_{PC} = 13.8$ Hz, $J_{PC} = 2.3$ Hz, C_{60} sp^3 π-bonded C); ^{31}P{H} NMR (122 MHz, CS_2/ext. CD_2Cl_2, 298 K): $\delta = 31.2$ (d, 1P, $^3J_{PP} = 12.8$ Hz), −16.3 (dd, 1P, $^3J_{PP} = 12.8$ Hz, $^3J_{PP} = 4.0$ Hz), −21.5 ppm (d, 1P, $^3J_{PP} = 4.0$ Hz); MS (FAB$^+$): m/z: 2210 [M^+].

X-ray crystal data for **3**: Greenish black crystals were obtained by slow diffusion of heptane into a solution of **3** in CS_2 at room temperature. The crystal used for data collection contained four molecules of CS_2 ($C_{102}H_{27}P_3O_6Ir_4{\cdot}4CS_2$, $M_r = 2210.09$): monoclinic, space group $P2_1/c$, $Z = 4$, $\rho_{calcd} = 2.141$ g cm^{-3}, $a = 17.472(5)$, $b = 20.071(6)$, $c = 22.639(6)$ Å, $\beta = 100.739(5)°$, $V = 7800(4)$ Å^3. The structure was solved by direct methods and refined by full-matrix least-squares analysis to give $R = 0.0422$ and $R_w = 0.0859$ (based on F^2) for 1144 parameters and 14530 unique reflections with $I > 2\sigma(I)$ and $1.69 < \theta < 25.52°$. Data was collected at $T = 293(2)$ K.

Received: November 10, 2003 [Z53290]

Keywords: cluster compounds · fullerenes · iridium · phosphanation · P ligands

---

[1] a) T. L. Makarova, B. Sundqvist, R. Höhne, P. Esquinazi, Y. Kopelevich, P. Scharff, V. A. Davydov, L. S. Kashevarova, A. V. Rakhmanina, *Nature* **2001**, *413*, 716–718; b) H. Imahori, H. Norieda, H. Yamada, Y. Nishimura, I. Yamazaki, Y. Sakata, S. Fukuzumi, *J. Am. Chem. Soc.* **2001**, *123*, 100–110; c) K. Hutchison, J. Schick, Y. Rubin, F. Wudl, *J. Am. Chem. Soc.* **1999**, *121*, 5611–5612.

[2] a) K. Lee, H. Song, J. T. Park, *Acc. Chem. Res.* **2003**, *36*, 78–86, and references therein; b) G. Lee, Y. J. Cho, B. K. Park, K. Lee, J. T. Park, *J. Am. Chem. Soc.* **2003**, *125*, 13920–13921; c) A. L. Balch, M. M. Olmstead, *Chem. Rev.* **1998**, *98*, 2123–2165; d) A. Stephens, M. L. H. Green, *Adv. Inorg. Chem.* **1997**, *44*, 1–43.

[3] a) X. R. Ye, Y. Lin, C. M. Wai, *Chem. Commun.* **2003**, 642–643; b) S. Hermans, J. Sloan, D. S. Shephard, B. F. G. Johnson, M. L. H. Green, *Chem. Commun.* **2002**, 276–277.

[4] A. J. Drakesmith, R. Whyman, *J. Chem. Soc. Dalton Trans.* **1973**, 362–367.

[5] R. M. S. Pereira, F. Y. Fijiwara, M. D. Vargas, D. Braga, F. Grepioni, *Organometallics* **1997**, *16*, 4833–4838, and references therein.

[6] A. J. Deeming, S. E. Kabir, N. L. Powel, P. A. Bates, M. B. Hursthouse, *J. Chem. Soc. Dalton Trans.* **1987**, 1529–1534.

[7] M. I. Bruce, P. A. Humphery, O. B. Shawkataly, M. R. Snow, E. R. T. Tiekink, W. R. Cullen, *Organometallics* **1990**, *9*, 2910–2919.

[8] a) C. Bianchini, P. Frediani, V. Sernau, *Organometallics* **1995**, *14*, 5458–5459; b) S. Hietkamp, H. Sommer, O. Stelzer, *Inorg. Synth.* **1989**, *25*, 120–122; c) J. G. Hartley, L. M. Venanzi, D. C. Goodall, *J. Chem. Soc.* **1963**, 3930–3936.

© 2004 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim