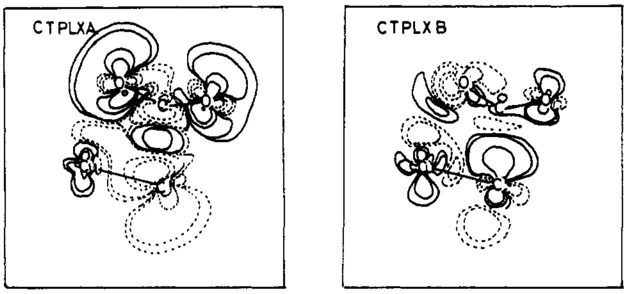

Figure 2. Difference density maps ($\Delta\rho = \rho$(CTPLXA) − ρ[Cu(CH_3)(PH_3)$_2$] − ρ[CO_2]) of CTPLXA and CTPLXB interactions:[17,18] (—) increase in density; (- - -) decrease in density.

of CH_3 and C of CO_2, as shown in Figure 2. The CTPLXB term,[18b] which includes charge transfer from CO_2 to Cu(CH_3)(PH_3)$_2$, accumulates electrons between Cu and O^α of CO_2.[18c] This is the first clear evidence that the CO_2 insertion proceeds via a four-center-like transition state.

Acknowledgment. This work was partially supported by the Ministry of Education, Culture and Science through a Grant-in-Aid for Co-operative Research (No. 6303002). The calculations were carried out at the Computer Center (Hitac M-680 and S-820 computers) of the Institute for Molecular Science under the Joint-Study Program.

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(18) (a) CTPLXA includes charge transfer from Cu(CH_3)(PH_3)$_2$ to CO_2 as a main contributor, polarization of CO_2, and their coupling terms. (b) CTPLXB includes charge transfer from CO_2 to Cu(CH_3)(PH_3)$_2$ as a main contributor, polarization of Cu(CH_3)(PH_3)$_2$, and their coupling term. (c) The difference density map of CTPLXB exhibits several complicated features; for instance, the electron density is increased in some regions between Cu and O^α atoms but is decreased in other regions between Cu and O^α atoms. These features are interpreted in terms of several orbital mixings, as follows: (i) The CO_2 nπ and π orbitals overlap with the empty Cu 4p_z orbital in a bonding way to form a charge transfer interaction, which would increase the electron density in the region of the Cu 4p_z orbital (rather far from Cu). (ii) At the same time, the CO_2 π and nπ orbitals overlap with the stable and doubly occupied Cu $d_z{}^2$ orbital in an antibonding way, which would decrease the density in the region of the Cu 3$d_z{}^2$ orbital (rather close to the Cu atom). (iii) CO_2 nπ and π orbitals form a charge transfer interaction with the Cu 4p_z orbital. In the virtual space, the Cu 4p_z orbital undergoes antibonding mixing with the more stable CO_2 nπ and π orbitals. This mixing enlarges the O^α p_π orbital but decreases the O^β p_π orbital in the virtual space, because the O p_π orbital has different phases in nπ and π orbitals. Thus, in the occupied space, the electron density decreases on the O^α atom but increases on the O^β atom, since orbital contribution in the occupied space is reverse to that in the virtual space. (iv) Because CTPLXB includes the polarization of the Cu(CH_3)(PH_3)$_2$ part, the electron cloud of this part is withdrawn toward the positively charged C atom, which would increase the electron density on the CH_3 ligand. A detailed discussion will be presented in our subsequent full paper.

Regioselectivity in Electrophilic Addition to a 3-Oxaplatina(II)cyclobutane Complex. Metallacycle Ring-Opening Reactions and Synthesis of a Platinum(IV) 3-Oxametallacyclobutane Complex

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Received September 28, 1989

Summary: Electrophilic addition to a 3-oxaplatina(II)cyclobutane complex is directed either to the metal or to the ring oxygen, depending on the nature of the electrophile. Reaction at the metal center gives a stable Pt(IV) oxametallacyclobutane complex, while reaction at the oxygen leads to ring-opened products.

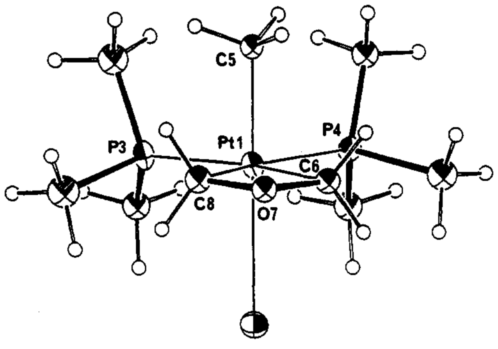
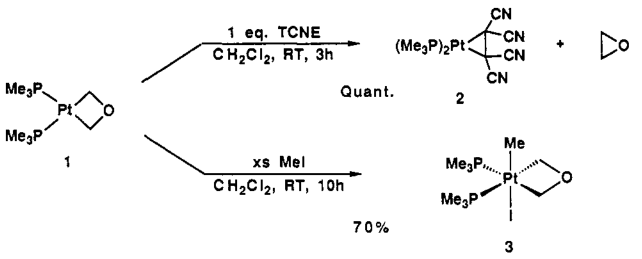


Figure 1. ORTEP drawing of 3. Selected bond distances (Å): Pt(1)–I(2), 2.771 (2); Pt(1)–C(5), 2.074 (24); Pt(1)–C(6), 2.106 (25); Pt(1)–C(8), 2.078 (25); Pt(1)–P(3), 2.372 (6); Pt(1)–P(4), 2.369 (6); C(6)–O(7), 1.50 (3); C(8)–O(7), 1.44 (3). Selected bond angles (deg): C(6)–Pt(1)–C(8), 66.5 (10); Pt(1)–C(6)–O(7), 93.9 (13); Pt(1)–C(8)–O(7), 97.2 (15); C(6)–O(7)–C(8), 102.4 (17); P(3)–Pt(1)–C(8), 97.1 (7); P(4)–Pt(1)–C(6), 95.9 (7); P(3)–Pt(1)–P(4), 100.6 (2); C(5)–Pt(1)–P(3), 92.2 (7); C(5)–Pt(1)–P(4), 91.3 (7); C(5)–Pt(1)–C(6), 88.9 (9); C(5)–Pt(1)–C(8), 86.8 (9); I(2)–Pt(1)–C(5), 175.7 (6); I(2)–Pt(1)–P(3), 90.50 (18); I(2)–Pt(1)–P(4), 91.54 (16); I(2)–Pt(1)–C(6), 87.6 (7); I(2)–Pt(1)–C(8), 89.6 (7). Least-squares dihedral plane angle (deg): [Pt(1)–C(8)–C(6)]–[C(6)–O(7)–C(8)], 1.1. Final residuals: $R(F) = 0.058$ and $R_w(F) = 0.057$.

Scheme I



We recently reported the first synthesis of the 3-oxametallacyclobutane structural class by dehydrative ring closure of an unprecedented bis(hydroxymethyl) complex of platinum(II).[2] Because of the extensive chemistry reported for all-carbon platinacyclobutanes,[3,4] these platinum complexes were considered ideal for probing the effect of noncoordinating oxygen substitution on metallacycle stability and reactivity. Here we report that oxaplatinacyclobutane complexes react with electrophiles with high selectivity in one of several reactivity manifolds, depending on the nature of the electrophile.

The trimethylphosphine-substituted 3-oxaplatina(II)cyclobutane complex 1 (Scheme I) was selected for initial investigation, maximizing electron density at the metal center and anticipating optimized stabilization of the Pt(IV) oxidation state. The reaction of complex 1 with 1 equiv of tetracyanoethylene (TCNE) at room temperature led, however, to reductive elimination of the metallacycle with quantitative formation of the known (Me_3P)$_2$Pt(TCNE) complex 2[5] and ethylene oxide as the

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[1] Du Pont Young Faculty Awardee, 1988–1989. Union Carbide Innovation Recognition Program Awardee, 1989.

(2) Hoover, J. F.; Stryker, J. M. *J. Am. Chem. Soc.* **1989**, *111*, 6466.

(3) Review: Puddephatt, R. J. *Coord. Chem. Rev.* **1980**, *33*, 149.

(4) Recent examples: (a) Ibers, J. A.; DiCosimo, R.; Whitesides, G. M. *Organometallics* **1982**, *1*, 13 and references therein. (b) Klingler, R. J.; Huffman, J. C.; Kochi, J. K. *J. Am. Chem. Soc.* **1982**, *104*, 2147 and references therein. (c) Wiberg, K. B.; McClusky, J. V.; Schulte, G. K. *Tetrahedron Lett.* **1986**, *27*, 3083. (d) Al-Essa, R. J.; Ling, S. S. M.; Puddephatt, R. J. *Organometallics* **1987**, *6*, 951 and references therein. (e) Neilsen, W. D.; Larsen, R. D.; Jennings, P. W. *J. Am. Chem. Soc.* **1988**, *110*, 3307 and references therein. (f) Chiu, K. W.; Henderson, W.; Kemmitt, R. D. W.; Prouse, L. J. S.; Russell, D. R. *J. Chem. Soc., Dalton Trans.* **1988**, 427 and references therein.

(5) Baddley, W. H. *Inorg. Chim. Acta, Rev.* **1968**, *2*, 7. Spectroscopic data: Clark, H. C.; Puddephatt, R. J. *Inorg. Chem.* **1971**, *10*, 416.

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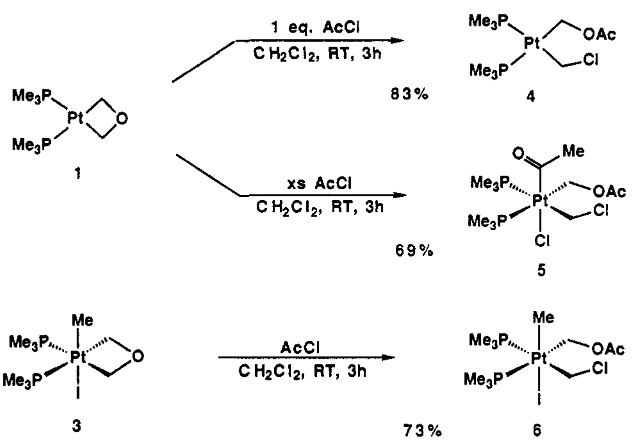
Scheme II



exclusive organic product. No nominally Pt(IV) intermediate or migratory insertion products were detected.

Oxidative addition with retention of the metallacycle was obtained on treatment of complex **1** with methyl iodide in dichloromethane at room temperature, providing the air-stable Pt(IV) oxametallacyclobutane **3** in 70% yield after purification from dichloromethane/ether.[6] The structure and stereochemistry assigned are fully consistent with the spectroscopic data; in particular, an upfield resonance at δ 4.9 (s, J_{PtC} = 647 Hz) in the $^{13}C\{^1H\}$ NMR spectrum for the Pt–Me carbon and a single upfield resonance at δ −51.90 (s, J_{PtP} = 1217 Hz) in the $^{31}P\{^1H\}$ NMR spectrum.[6] The conformation of the metallacyclobutane ring in the solid state was determined by X-ray crystallography (Figure 1).[7] The dihedral angle between the planes defined by atoms [C(6)–Pt(1)–C(8)] and [C(6)–O(7)–C(8)] is calculated to be 1.1°, although such minor deviation from planarity is not statistically significant. Ring puckering in other structurally characterized Pt(IV) metallacyclobutane complexes range from 0° to as great as 28°,[4b,8] and the corresponding bis(triphenylphosphine)-3-oxaplatina(II)cyclobutane[2] ring is also essentially planar. Surprisingly, the metal–carbon bond lengths in the Pt(IV) metallacycle are longer than those in the Pt(II) complex; the bond length contraction expected on oxidation of the metal is apparently overwhelmed by the stronger trans influence of the trimethylphosphine ligands in **3** compared to that of the triphenylphosphine ligands in the Pt(II) complex.

In contrast to the reaction with methyl iodide, treatment of complex **1** with 1 equiv of acetyl chloride led to exclusive attack at the metallacycle oxygen (Scheme II), giving ring-opened Pt(II) complex **4**, isolated in 83% yield after recrystallization from ether/hexane.[9] No evidence for competitive addition to the metal was observed. The lack of symmetry was readily apparent from spectroscopic characterization, which indicated inequivalent methylene groups in both the ^1H and $^{13}C\{^1H\}$ NMR spectra and inequivalent phosphines in the $^{31}P\{^1H\}$ NMR spectrum.[9] The carbonyl absorption at 1715 cm^{-1} in the infrared spectrum is significantly higher in energy than expected for a Pt(IV) acyl complex.[10] Treatment of complex **1** with an excess of acetyl chloride gave both ring opening and oxidative addition, forming Pt(IV) acyl complex **5** in 69% yield after recrystallization from dichloromethane/ether.[11,12] This complex displayed both metal–acyl (1670 cm^{-1}) and organic acetate (1725 cm^{-1}) bands in the infrared spectrum and characteristic diastereotopic methylene hydrogens in the ^1H NMR spectrum. Similarly, methyl iodide adduct **3** also undergoes facile metallacycle cleavage with acetyl chloride, giving the analogous Pt(IV) complex **6** in 73% yield after purification.[13]

The high level of selectivity exhibited in these reactions is indicative of the extent to which reactivity can be manipulated in such "polyfunctional" organometallic systems. It is attractive to formulate the chemoselectivity for metal versus oxygen addition in terms of hard and soft acid–base principles,[14] with the weakly electrophilic methyl iodide reacting preferentially at the relatively soft Pt(II) center

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[6] Data for complex **3**: mp 149–150 °C (sealed under vacuum, no decomposition); IR (KBr) 2980, 2910, 2815, 1430, 1290, 1250, 1205, 1195, 965, 950, 915, 740 cm^{-1}; ^1H NMR (300 MHz, C_6D_6) δ 5.44 (m, J_{PtH} = 81.7 Hz, 2 H), 3.71 (m, J_{PtH} = 39.5 Hz, 2 H), 1.34 (t, J_{PH} = 7.6 Hz, J_{PtH} = 71.5 Hz, 3 H), 0.84 (d, J_{PH} = 8.2 Hz, J_{PtH} = 11.7 Hz, 18 H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 29.8 (d, J_{PC} = 115 Hz, J_{PtC} = 378 Hz), 14.2 (m), 4.9 (s, J_{PtC} = 647 Hz); $^{31}P\{^1H\}$ NMR (146 MHz, $CDCl_3$) δ −51.90 (s, J_{PtP} = 1217 Hz). Anal. Calcd for $C_9H_{25}IOP_2Pt$: C, 20.27; H, 4.73. Found: C, 20.34; H, 4.78.

[7] An irregularly shaped but diffractable single crystal of a CH_2Cl_2 solvate was obtained by cleaving a needle obtained by recrystallization from CH_2Cl_2/Et_2O. X-ray crystallography was carried out at −156 °C by Dr. William E. Streib at the Indiana University Department of Chemistry Molecular Structure Center. Crystal data for complex **3**: $PtC_{10}H_{27}OP_2ICl_2$: space group $P2_1$; cell dimensions (at −156 °C) a = 7.557 (2) Å, b = 11.140 (3) Å, c = 11.194 (3) Å, β = 94.22 (1)°; Z (molecules/cell) = 2; V = 939.83 Å^3; d(calcd) = 2.184 g cm^{-3}; wavelength 0.71069 Å; linear absorption coefficient 96.128 cm^{-1}. The structure was solved by using a combination of direct methods and Fourier techniques and was refined to final residuals $R(F)$ = 0.058 and $R_w(F)$ = 0.057 for 2288 independent reflections ($F > 3.00\sigma(F)$) of 2462 unique intensities collected in the range $6.0° \leq 2\theta \leq 45.0°$. Details of the data collection and structure solution, atomic positional and thermal parameters, complete bond distance and angle data, and a listing of F_o vs F_c are included as supplementary information or may be obtained directly from the Molecular Structure Center. Request Report No. 88210.

[8] See: Burton, J. T.; Puddephatt, R. J.; Jones, N. L.; Ibers, J. A. *Organometallics* **1983**, *2*, 1487 and references therein.

[9] Data for complex **4**: mp 103–104 °C (sealed under nitrogen, no decomposition); IR (KBr) 2990, 2910, 1715, 1530, 1420, 1360, 1280, 1210, 1010, 950, 850, 720, 670 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.77 (dd, J_{PH} = 7.5, 3.6 Hz, J_{PtH} = 50.9 Hz, 2 H), 3.74 (dd, J_{PH} = 9.9, 2.2 Hz, J_{PtH} = 40.4 Hz, 2 H), 1.99 (s, 3 H), 1.54 (d, J_{PH} = 8.6 Hz, J_{PtH} = 19.2 Hz, 9 H), 1.50 (d, J_{PH} = 8.7 Hz, J_{PtH} = 20.4 Hz, 9 H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 173.0 (d, J_{PC} = 4.5 Hz, J_{PtC} = 38.6 Hz), 63.6 (dd, J_{PC} = 117, 7.7 Hz, J_{PtC} = 764 Hz), 38.7 (dd, J_{PC} = 118, 8.6 Hz, J_{PtC} = 773 Hz), 21.7 (s), 16.3 (m); $^{31}P\{^1H\}$ NMR (146 MHz, $CDCl_3$) δ −23.45 (d, J_{PP} = 13.7 Hz, J_{PtP} = 1772 Hz), −24.63 (d, J_{PP} = 13.8 Hz, J_{PtP} = 1858 Hz). Anal. Calcd for $C_{10}H_{25}ClO_2P_2Pt$: C, 25.57; H, 5.36. Found: C, 25.65; H, 5.34.

[10] $(Me_2PPh)_2Pt(Me)_2(COMe)Cl$: Ruddick, J. D.; Shaw, B. L. *J. Chem. Soc. A* **1969**, 2801.

[11] Data for complex **5**: mp 149–150 °C dec (sealed under vacuum); IR (KBr) 2960, 1725, 1670, 1420, 1350, 1290, 1210, 1170, 1090, 1020, 950, 890, 860, 740, 650 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.18 (ddd, J_{HH} = 7.8 Hz, J_{PH} = 5.1, 3.1 Hz, J_{PtH} = 55.1 Hz, 1 H), 4.85 (dt, $J_{HH} \approx J_{PH}$ = 7.5 Hz, J_{PH} = 1.8 Hz, J_{PtH} = 40.2 Hz, 1 H), 4.29 (ddd, J_{HH} = 8.6 Hz, J_{PH} = 6.5, 1.9 Hz, J_{PtH} = 66.0 Hz, 1 H), 4.06 (ddd, J_{HH} = 8.2 Hz, J_{PH} = 5.3, 3.3 Hz, J_{PtH} = 38.7 Hz, 1 H), 2.31 (s, J_{PtH} = 10.9 Hz, 3 H), 2.06 (s, 3 H), 1.65 (d, J_{PH} = 10.9 Hz, J_{PtH} = 11.3 Hz, 9 H), 1.59 (d, J_{PH} = 10.2 Hz, J_{PtH} = 12.1 Hz, 9 H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 191.9 (s, J_{PtC} = 822 Hz), 171.3 (d, J_{PC} = 5.0 Hz, J_{PtC} = 22.4 Hz), 56.3 (d, J_{PC} = 109 Hz, J_{PtC} = 653 Hz), 36.2 (m), 35.2 (d, J_{PC} = 133 Hz, J_{PtC} = 695 Hz), 21.1 (s), 13.7 (m); $^{31}P\{^1H\}$ NMR (146 MHz, $CDCl_3$) δ −30.99 (d, J_{PP} = 19.9 Hz, J_{PtP} = 1498 Hz), −33.15 (d, J_{PP} = 20.0 Hz, J_{PtP} = 1509 Hz). Anal. Calcd for $C_{12}H_{28}Cl_2O_3P_2Pt$: C, 26.29; H, 5.15. Found: C, 26.17; H, 5.21.

[12] Reaction of the purified ring-opened complex **4** with acetyl chloride also produces some acyl complex **5**; however, this reaction is complicated by solvolytic side reactions. See: McCrindle, R.; Arsenault, G. J.; Farwaha, R. J.; Hampden-Smith, M. J.; McAlees, A. J. *J. Chem. Soc., Chem. Commun.* **1986**, 943.

[13] Data for complex **6**: mp 92–94 °C (sealed under vacuum, no decomposition); IR (KBr) 3000, 2940, 1715, 1420, 1370, 1295, 1245, 1210, 1020, 955, 860, 740, 660 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.02 (dt, $J_{HH} \approx J_{PH}$ = 8.2 Hz, J_{PH} = 2.1 Hz, J_{PtH} = 54.7 Hz, 1 H), 4.81 (dt, $J_{HH} \approx J_{PH}$ = 6.8 Hz, J_{PH} = 3.3 Hz, J_{PtH} = 50.6 Hz, 1 H), 4.57 (dt, $J_{HH} \approx J_{PH}$ = 9.0 Hz, J_{PH} = 1.6 Hz, J_{PtH} = 62.9 Hz, 1 H), 4.06 (ddd, J_{HH} = 10.9 Hz, J_{PH} = 6.8, 4.1 Hz, J_{PtH} = 48.4 Hz, 1 H), 2.05 (s, 3 H), 1.71 (d, J_{PH} = 2.7 Hz, J_{PtH} = 12.1 Hz, 9 H), 1.68 (d, J_{PH} = 1.9 Hz, J_{PtH} = 10.9 Hz, 9 H), 0.95 (t, J_{PH} = 6.1 Hz, J_{PtH} = 67.6 Hz, 3 H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 171.6 (d, J_{PC} = 4.6 Hz, J_{PtC} = 23.6 Hz), 52.8 (d, J_{PC} = 144 Hz, J_{PtC} = 605 Hz), 28.9 (d, J_{PC} = 151 Hz, J_{PtC} = 639 Hz), 21.2 (s), 15.4 (d, J_{PC} = 30.5 Hz, J_{PtC} = 234 Hz), 14.6 (d, J_{PC} = 30.2 Hz, J_{PtC} = 221 Hz), 6.8 (m, J_{PtC} = 605 Hz); $^{31}P\{^1H\}$ NMR (146 MHz, $CDCl_3$) δ −46.91 (d, J_{PP} = 14.9 Hz, J_{PtP} = 1352 Hz), −48.66 (d, J_{PP} = 15.0 Hz, J_{PtP} = 1248 Hz). Anal. Calcd for $C_{11}H_{28}ClIO_2P_2Pt$: C, 21.60; H, 4.61. Found: C, 21.18; H, 4.62.

[14] Review: Ho, T.-L. *Tetrahedron* **1985**, *41*, 3.

and the more strongly electrophilic acetyl chloride kinetically attacking the hard ring oxygen. The reactivity observed on treatment with TCNE is somewhat more difficult to rationalize; the possibility that the reductive elimination of ethylene oxide is triggered not by coordination of the olefin but by one-electron oxidation of the metal center is currently under investigation.

Acknowledgment. We thank Dr. William Streib for the X-ray crystal structure determination. Financial support from the donors of the Petroleum Research Fund, administered by the American Chemical Society, and from Union Carbide Corp. is gratefully acknowledged.

Supplementary Material Available: Details of the data collection and structure solution and listings of atomic positional and thermal parameters, complete bond distance and angle data and least-squares planes (12 pages); a listing of F_o vs F_c (6 pages). Ordering information is given on any current masthead page.

C-H Addition Followed by Alkyne Insertion into the Metal-Hydrogen Bond of an Iridium Complex

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Summary: Thermal C-H activation of benzene is observed with $[Ir(COD)(PMe_3)_3]Cl$ leading to the formation of *mer*-$IrH(Ph)(Cl)(PMe_3)_3$ (**1**). **1** will undergo further reaction with 2-butyne upon chloride removal to yield $[Ir(Ph)(methallyl)(PMe_3)_3][PF_6]$ (**2**). **2** has been characterized by X-ray crystallography. Insertion of 2-butyne into the Ir-H bond of **1** followed by β-hydride elimination to yield an (allene)hydridoiridium complex appear to be key features in the formation of **2**. This reaction sequence brings us a step closer to fully functionalizing hydrocarbons following C-H addition.

The marked activity in the area of carbon-hydrogen bond cleavage at transition-metal centers (C-H activation) has led to the discovery of literally dozens of systems that are capable of adding alkane and arene C-H bonds.[1] However, with a few notable exceptions,[2] the chemistry stops at the initial C-H addition step: attempts to functionalize the metal hydrocarbyl fragment for the most part have been unsuccessful. There are many reasons for this lack of success, but most prominent among them is the nature of the hydridometal hydrocarbon grouping. In many cases, addition of reagents intended to induce further reaction of the complex results in reductive elimination to nonproductively re-form the original hydrocarbon.[3] This communication reports on a system in which further reactions of the C-Ir-H species formed by addition of a C-H bond to an iridium complex are made facile by chemical removal of a chloride ligand.

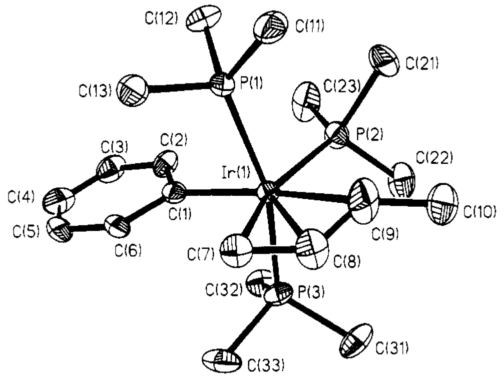
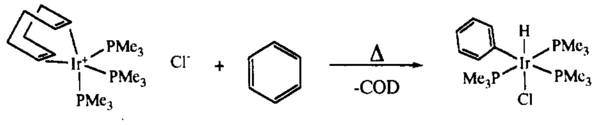


Figure 1. ORTEP plot of the phenyl(methallyl)tris(trimethylphosphine)iridium cation of **2**. Important bond distances (Å): Ir(1)-P(1) = 2.351 (2), Ir(1)-P(2) = 2.328 (2), Ir(1)-P(3) = 2.350 (2), Ir(1)-C(1) = 2.118 (6), Ir(1)-C(7) = 2.208 (7), Ir(1)-C(8) = 2.190 (9), Ir(1)-C(9) = 2.36 (1), C(7)-C(8) = 1.35 (1), C(8)-C(9) = 1.27 (1), C(9)-C(10) = 1.44 (1). Important bond angles (deg): P(1)-Ir(1)-P(2) = 93.0 (1), P(1)-Ir(1)-P(3) = 163.3 (1), P(2)-Ir(1)-P(3) = 94.0 (1), P(1)-Ir(1)-C(1) = 82.3 (2), P(2)-Ir(1)-C(1) = 104.2 (2), P(3)-Ir(1)-C(1) = 81.2 (2), P(1)-Ir(1)-C(7) = 88.0 (2), P(2)-Ir(1)-C(7) = 156.6 (2), P(3)-Ir(1)-C(7) = 91.6 (2), P(1)-Ir(1)-C(8) = 101.2 (3), P(2)-Ir(1)-C(8) = 121.6 (3), P(3)-Ir(1)-C(8) = 88.0 (3), P(1)-Ir(1)-C(9) = 62.6 (3), P(2)-Ir(1)-C(9) = 91.7 (3), P(3)-Ir(1)-C(9) = 102.3 (3), Ir(1)-C(7)-C(8) = 71.3 (5), C(7)-C(8)-C(9) = 138.6 (10) C(8)-C(9)-C(10) = 135.4 (10).

Heating a slurry of tris(trimethylphosphine)(cyclooctadiene)iridium chloride,[4] $[Ir(COD)(PMe_3)_3]Cl$, in benzene leads to loss of cyclooctadiene and the addition of benzene to yield *mer*-hydridophenylchlorotris(trimethylphosphine)iridium, $Ir(H)(Ph)(Cl)(PMe_3)_3$ (**1**) (eq 1).



(1)

Compound **1** was identified on the basis of its elemental analysis, ^1H and ^{13}C NMR spectra, and single-crystal X-ray structure.[5] One interesting feature of **1** is an extremely large barrier to rotation about the iridium-phenyl bond as evidenced by the inequivalence of all five phenyl hydrogens in the ^1H NMR spectrum and all six phenyl carbons in the ^{13}C NMR spectrum. This feature will be

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(1) Some important references are: (a) Shilov, A. E. *Activation of Saturated Hydrocarbons by Transition Metal Complexes*; D. Reidel: Hingham, MA, 1984, and references therein. (b) Bergman, R. G. *Science* **1984**, *223*, 902. (c) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245. (d) Janowicz, A. H.; Periana, R. A.; Buchanan, J. M.; Kovac, C. M.; Stryker, J. M.; Wax, M. J.; Bergman, R. G. *Pure Appl. Chem.* **1984**, *56*, 13. (e) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1986**, *108*, 4814. (f) Ghosh, C. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1987**, *109*, 4726. (g) Hackett, M.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 1449. (h) Jones, W. D.; Feher, F. J. *Acc. Chem. Res.* **1989**, *22*, 91.

(2) Some references on functionalization in systems involving oxidative addition of a C-H bond are: (a) Crabtree, R. H.; Parnell, C. P.; Uriarte, R. J. *Organometallics* **1987**, *6*, 696. (b) Felkin, H.; Fillebeen-Khan, T.; Gault, Y.; Holmes-Smith, R.; Zakrzewski, J. *Tetrahedron Lett.* **1984**, 1279. (c) Jones, W. D.; Kosar, W. P. *J. Am. Chem. Soc.* **1986**, *108*, 5640. (d) Fisher, B. J.; Eisenberg, R. *Organometallics* **1983**, *2*, 764. (e) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7332. (f) Jones, W. D.; Foster, G. P.; Putinas, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 5047. (g) Jordan, R. F.; Taylor, D. F. *J. Am. Chem. Soc.* **1989**, *111*, 778. (h) Ghosh, C. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1989**, *111*, 375.

(3) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 3929.

(4) Merola, J. S.; Kacmarcik, R. T. *Organometallics* **1989**, *8*, 778.

(5) Approximately 1.0 g (1.77 mmol) of $[Ir(COD)(PMe_3)_3]Cl$ was slurried in 50 mL of benzene and sealed in a pressure tube. The slurry was heated to 150 °C overnight, at which time all material had dissolved to yield a pale yellow solution. Removal of the benzene under vacuum yielded a pale yellow solid. Washing of the solid with small amounts of pentane removed what appears to be a low yield of *fac*-$IrH(Ph)(Cl)(PMe_3)_3$ identified only by ^1H NMR spectroscopy. The bulk of the material was 0.55 g (1.03 mmol, 58% yield) of *mer*-$IrH(Ph)(Cl)(PMe_3)_3$ (**1**), a pentane-insoluble off-white solid. Anal. Calcd (found) for $C_{15}H_{33}ClIrP_3$: C, 33.74 (33.35); H, 6.23 (6.25); Cl, 6.64 (6.91); Ir, 35.99 (36.05); P, 17.40 (16.98). ^1H NMR (C_6D_6): δ −23.46 (q, J_{P-H} = 4.6 Hz, 1 H, Ir-H), 1.23 (t, J_{P-H} = 2.9 Hz, 18 H, trans PMe_3), 1.58 (d, J_{P-H} = 7.7 Hz, 9 H, cis PMe_3), 6.7-6.9 (complex set of three pseudotriplets, 3 H, phenyl), 7.39 (pseudotriplet, 1 H, phenyl), 8.15 (pseudotriplet, 1 H, phenyl). The single-crystal X-ray structure of **1** confirmed the *mer* stereochemistry. Details of the structure determination will be included in the full paper.

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