Synthesis of Iridaoxacyclohexadiene and Iridacyclopentenone Complexes via C–H Bond Activation

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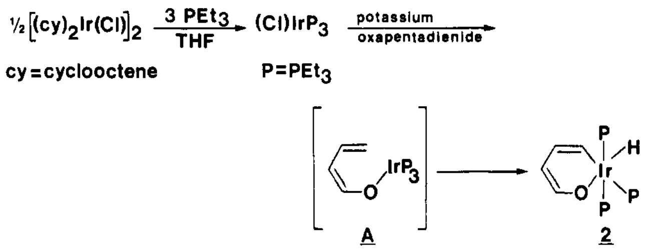
Received September 19, 1990

Summary: Treatment of $(Cl)Ir(PEt_3)_3$ with potassium oxapentadienide produces the novel metallacyclohexadiene ("metallapyran") complex *mer*-$(IrCH{=}CHCH{=}CHO)(PEt_3)_3(H)$ (**2**) via metal-centered C–H bond activation. In contrast, treatment of "$(Cl)Ir(PMe_3)_3$" with oxapentadienide yields $(IrOCH{=}CHCH{=}CH_2)(PMe_3)_3$ (**3**), which quickly rearranges to the η^3-oxapentadienyl complex $(\eta^3\text{-}CH_2\cdots CH\cdots CHCH{=}O)Ir(PMe_3)_3$ (**4**). When it is refluxed in acetone, **4** undergoes aldehydic C–H bond activation, producing the metallacyclopentenone complex *fac*-$(IrCH_2CH{=}CHC{=}O)(PMe_3)_3(H)$ (**5**).

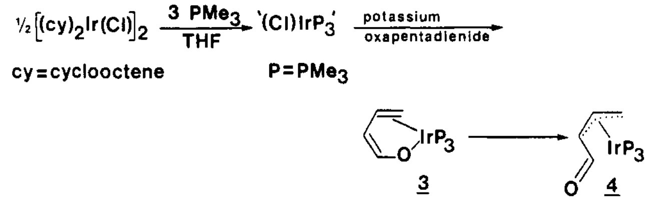
Earlier, we reported a new synthetic approach to metallacyclohexadiene complexes, which utilized pentadienide as the source of ring carbon atoms.[1] In the prototypical reaction, we showed that $(Cl)Ir(PEt_3)_3$ reacts cleanly with potassium 2,4-dimethylpentadienide to produce the iridacyclohexadiene complex $(IrCH{=}C(Me)CH{=}C(Me)CH_2)(PEt_3)_3(H)$ (1) via metal-centered activation of a pentadienyl C–H bond.[1a] We now report that oxapentadienide reagents can be used in an analogous fashion to produce novel metallaoxacyclohexadiene ("metallapyran")[3] and metallacyclopentenone[4] complexes.

Treatment of $(Cl)Ir(PEt_3)_3$[5] with potassium oxapentadienide[6] yields the iridapyran complex $(IrCH{=}CHCH{=}CHO)(PEt_3)_3(H)$ (2; Scheme I).[7] Although mechanistic details of this reaction are still sketchy, it seems probable that the key intermediate is the 16e oxy-

Scheme I



Scheme II



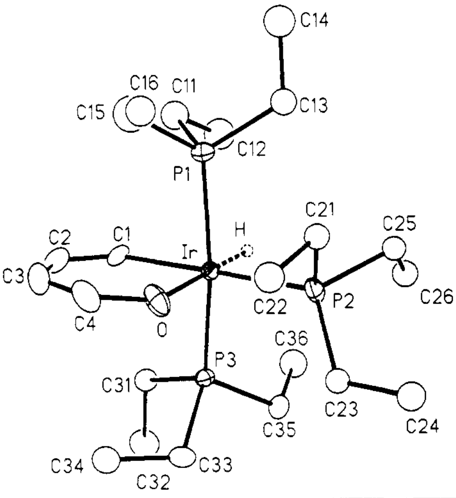


Figure 1. ORTEP drawing of *mer*-$(IrCH{=}CHCH{=}CHO)(PEt_3)_3(H)$ (2). Bond distances (Å): Ir–P1, 2.318 (3); Ir–P2, 2.368 (3); Ir–P3, 2.330 (3); Ir–C1, 2.072 (12); Ir–O, 2.172 (9); C1–C2, 1.350 (21); C2–C3, 1.449 (31); C3–C4, 1.327 (33); C4–O, 1.317 (16). Bond angles (deg): P1–Ir–P2, 98.6 (1); P1–Ir–P3, 161.1 (1); P2–Ir–P3, 96.4 (1); P1–Ir–O, 98.2 (2); P2–Ir–O, 83.6 (2); P3–Ir–O, 94.8 (2); P1–Ir–C1, 80.4 (4); P2–Ir–C1, 174.0 (4); P3–Ir–C1, 85.7 (3); O–Ir–C1, 90.7 (4); Ir–C1–C2, 123.3 (12); C1–C2–C3, 127.7 (16); C2–C3–C4, 126.1 (14); C3–C4–O, 129.6 (17); C4–O–Ir, 122.3 (11).

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[1] Metallacyclohexadiene and Metallabenzene Chemistry. 4. For previous papers in this series, see: (a) Bleeke, J. R.; Peng, W.-J. *Organometallics* **1987**, *6*, 1576. (b) Bleeke, J. R.; Xie, Y.-F.; Peng, W.-J.; Chiang, M. *J. Am. Chem. Soc.* **1989**, *111*, 4118. (c) Bleeke, J. R.; Peng, W.-J.; Xie, Y.-F.; Chiang, M. Y. *Organometallics* **1990**, *9*, 1113.

[2] Pentadienyl–Metal–Phosphine Chemistry. 22. For recent papers in this series, see: (a) Bleeke, J. R.; Wittenbrink, R. J.; Clayton, T. W., Jr. *J. Am. Chem. Soc.* **1990**, *112*, 6539. (b) Bleeke, J. R.; Rauscher, D. J. *J. Am. Chem. Soc.* **1989**, *111*, 8972.

[3] The metallapyran ring skeleton is extremely rare and has not previously been structurally characterized. For a recent report of a zirconium-based metallapyran, see: Erker, G.; Petrenz, R. *J. Chem. Soc., Chem. Commun.* **1989**, 345. Related to these complexes are the cyclometalated *o*-phenylphenoxide systems of Rothwell. See, for example: (a) Kerschner, J. L.; Rothwell, I. P.; Hoffman, J. C.; Streib, W. E. *Organometallics* **1988**, *7*, 1871. (b) Steffey, B. D.; Chamberlain, L. R.; Chesnut, R. W.; Chebi, D. E.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1989**, *8*, 1419.

[4] For other examples of complexes containing the metallacyclopentenone ring skeleton, see: (a) Huffman, M. A.; Liesbeskind, L. S.; Pennington, W. T., Jr. *Organometallics* **1990**, *9*, 2194. (b) Mitsudo, T.; Watanabe, H.; Sasaki, T.; Takegami, Y.; Watanabe, Y.; Kafuku, K.; Nakatsu, K. *Organometallics* **1989**, *8*, 368. (c) Navarre, D.; Rudler, H.; Daran, J. C. *J. Organomet. Chem.* **1986**, *314*, C34. (d) Cotton, F. A.; Troup, J. M.; Billups, W. E.; Lin, L. P.; Smith, C. V. *J. Organomet. Chem.* **1975**, *102*, 345.

[5] Produced in situ via the reaction of $[(cyclooctene)_2IrCl]_2$ with 6 equiv of PEt_3 in tetrahydrofuran. $^{31}P\{^1H\}$ NMR spectroscopy (C_4D_8O, 22 °C, 121 MHz) indicated the presence of a single species: δ 15.4 (d, J_{P-P} = 24 Hz, 2), 5.8 (t, J_{P-P} = 24 Hz, 1) (signals are referenced to H_3PO_4).

[6] Produced via the reaction of crotonaldehyde with potassium amide in liquid ammonia: Heiszwolf, G. J.; Kloosterziel, H. *Recl. Trav. Chim. Pays-Bas* **1967**, *86*, 807.

[7] Synthesis of 2: Under nitrogen, triethylphosphine (0.40 g, 3.4 mmol) was added dropwise to a cold (0 °C) stirred solution of $[(cyclooctene)_2Ir(Cl)]_2$ (0.50 g, 0.56 mmol) in 15 mL of tetrahydrofuran (THF). Potassium oxapentadienide (0.22 g, 2.0 mmol) in 15 mL of THF was then added dropwise. The solution was warmed to room temperature and stirred overnight, before removal of the THF solvent. 2 was extracted from the resulting residue with pentane and crystallized at -30 °C from a concentrated pentane solution containing several drops of acetone; yield (orange crystals) 0.55 g, 80%. Anal. Calcd for $C_{22}H_{50}IrOP_3$: C, 42.90; H, 8.20. Found: C, 42.97; H, 8.21.

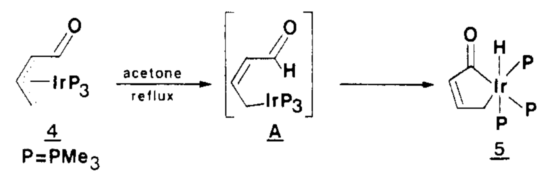
0276-7333/91/2310-0019$02.50/0

gen-bound η^1-oxapentadienyl species (A, Scheme I), which undergoes intramolecular oxidative addition across the sp^2 C–H bond on the chain terminus. The solid-state structure of **2**, derived from a single-crystal X-ray diffraction study, is shown in Figure 1.[8] Compound **2** is isostructural with its metallacyclohexadiene analogue **1**.[1a] The six-membered ring is essentially planar (mean deviation 0.024 Å) and exhibits the expected alternation in C–C bond lengths. The ring C–O bond, formally a C–O single bond, is unusually short (1.317 (16) Å)[9] and may reflect some participation by an oxygen lone pair in ring π-bonding. The compound adopts an octahedral coordination geometry in which the hydride ligand resides cis to C1 (the carbon atom to which it was originally bonded) and trans to the ring oxygen atom. The phosphines fill the remaining three coordination sites, adopting a *mer* arrangement. Due to the planarity of the metallacycle, the two mutually trans phosphines are equivalent and give rise to a characteristic doublet–triplet pattern in the $^{31}P\{^1H\}$ NMR spectrum.[10]

A close comparison of the ^{13}C and ^1H NMR spectra of **2**[10] with those of its metallacyclohexadiene analogue **1**[1a] reveals some interesting differences. In the $^{13}C\{^1H\}$ NMR spectrum of **2**, ring carbon C4 appears at δ 149.6 and is shifted substantially downfield from its position in **1**, while C3 appears at δ 99.7 and is shifted upfield. These shifts result from the perturbation of the charge distribution in the ring in **2**, caused by the presence of the electronegative oxygen atom. The oxygen atom causes the α-C atom (C4) to be more positive and the β-C atom to be more negative than the corresponding atoms in **1**. In the ^1H NMR spectrum of **2**, the iridium–hydride signal is shifted dramatically upfield from its position in **1** (δ −24.9 vs δ −13.1). Again, this shift apparently results from the hydride's trans relationship to O in **2** vs C in **1**.

When "$(Cl)Ir(PMe_3)_3$"[11] is substituted for $(Cl)Ir(PEt_3)_3$ in the above reaction system, a rather different chemistry is observed. As shown in Scheme II, the initial product of this reaction is $(\overline{\mathrm{IrOCH{=}CHCH{=}CH}}_2)(PMe_3)_3$ (**3**), which has been unambiguously identified from its NMR spectra.[12] Particularly diagnostic are the phosphorus-coupled signals at δ 42.6 and 23.8 in the $^{13}C\{^1H\}$ NMR spectrum, which are due to the metal-coordinated olefin carbons. The $^{31}P\{^1H\}$ NMR spectrum of **3** consists of three doublet of doublet patterns. Compound **3** cannot be isolated in pure form because in solution it quickly (over a period of several hours at room temperature) rearranges to the η^3-oxapentadienyl complex $(\eta^3\text{-}CH_2\cdots CH\cdots CHCH{=}O)Ir(PMe_3)_3$ (**4**; Scheme II).[13,14] This species can be isolated and crystallized in pure form from pentane.[15]

Scheme III



4
P=PMe3

A

5

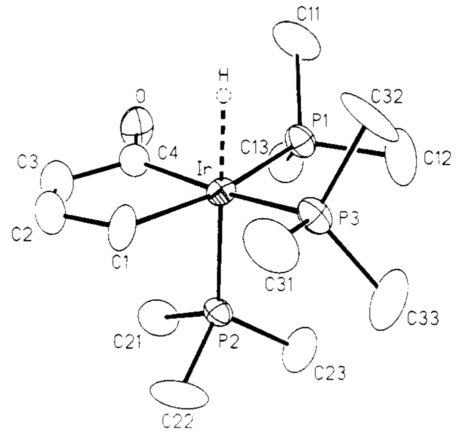


Figure 2. ORTEP drawing of *fac*-$(\overline{\mathrm{IrCH_2CH{=}CHC}}{=}O)(PMe_3)_3(H)$ (**5**). Bond distances (Å): Ir–P1, 2.298 (4); Ir–P2, 2.337 (4); Ir–P3, 2.333 (3); Ir–C1, 2.163 (19); Ir–C4, 2.075 (13); C1–C2, 1.446 (24); C2–C3, 1.339 (27); C3–C4, 1.492 (30); C4–O, 1.219 (16). Bond angles (deg): P1–Ir–P2, 97.2 (2), P1–Ir–P3, 98.3 (1); P2–Ir–P3, 98.6 (1); P1–Ir–C1, 168.4 (4); P2–Ir–C1, 87.9 (5); P3–Ir–C1, 91.1 (4); P1–Ir–C4, 89.7 (4); P2–Ir–C4, 90.6 (4); P3–Ir–C4, 166.9 (5); C1–Ir–C4, 79.9 (6); Ir–C1–C2, 109.8 (11); C1–C2–C3, 121.1 (19); C2–C3–C4, 115.1 (17); C3–C4–Ir, 113.7 (10); C3–C4–O, 116.3 (14); Ir–C4–O, 129.9 (13).

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(8) Crystal data for **2**: orange-yellow prism, 0.35 × 0.38 × 0.45 mm; monoclinic, space group $P2_1/n$, a = 9.830 (2) Å, b = 16.241 (3) Å, c = 17.100 (2) Å, β = 101.00 (1)°, V = 2679.8 (8) Å^3, Z = 4, d_{calcd} = 1.526 g/cm^3, μ = 51.50 cm^{-1}; Siemens R3m/V diffractometer, graphite-monochromated Mo Kα radiation, 22 °C, $\theta/2\theta$ scanning technique; 6187 unique reflections with $3.5 < 2\theta < 55°$ collected, 3741 reflections with $I > 3\sigma(I)$ used in refinement; semiempirical absorption correction (ψ scans); R = 4.25%, R_w = 5.72%, GOF = 1.11, data-to-parameter ratio 24.1:1. Note: The ethyl groups on P2 exhibited a 2-fold disorder, which was successfully modeled with site occupancy factors of 63 (1)% and 37 (1)% for the major and minor conformers. Disorder was also observed for one methyl group (C16) on P1; site occupancy factors of 67 (2)% and 33 (2)% were refined. The location of the hydride ligand was inferred from the positions of the heavy atoms in the molecule. In Figure 1, it was placed at an idealized position with Ir–H = 1.75 Å and angle O–Ir–H = 180°.

(9) A normal C–O single-bond length is 1.43 Å.

(10) Spectroscopic data for **2** (carbon atoms in the chain are numbered by starting from the end opposite oxygen): ^1H NMR (C_6D_6, 22 °C, 300 MHz) δ 6.92 (br s, 2, H2 and H4), 6.80 (br s, 1, H1), 4.87 (t, J = 6.0 Hz, 1, H3), 2.01–1.57 (m, 18, PEt_3 CH_2's), 1.08–0.75 (m, 27, PEt_3 CH_3's), −24.94 (t of d, J_{H-P} = 28.0, 16.7 Hz, 1, Ir–H); $^{13}C\{^1H\}$ NMR (C_6D_6, 22 °C, 75 MHz) δ 149.6 (s, C4), 122.4 (s, C2), 117.3 (d of t, J_{C-P} = 76.9 Hz, 16.4 Hz, C1), 99.7 (s, C3), 20.0 (d, J_{C-P} = 21.9 Hz, PEt_3 CH_2's), 17.2 (virtual t, J_{C-P} = 31.3 Hz, mutually trans PEt_3 CH_2's), 8.4 (d, J_{C-P} = 18.7 Hz, PEt_3 CH_3's); $^{31}P\{^1H\}$ NMR (C_6D_6, 22 °C, 121 MHz, referenced to H_3PO_4) δ −7.7 (d, J_{P-P} = 16.8 Hz, 2), −19.8 (t, J_{P-P} = 16.8 Hz, 1).

(11) Produced in situ via the reaction of $[(cyclooctene)_2IrCl]_2$ with 6 equiv of PMe_3 in tetrahydrofuran. $^{31}P\{^1H\}$ NMR spectroscopy indicated the presence of several iridium–phosphine complexes, probably including $(cyclooctene)Ir(PMe_3)_3(Cl)$: (a) Herskovitz, T.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1976**, *98*, 1615. (b) Herskovitz, T. *Inorg. Synth.* **1982**, *21*, 99.

(12) Spectroscopic data for **3** (carbon atoms in the chain are numbered by starting from the end opposite oxygen): ^1H NMR (C_6D_6, 22 °C, 300 MHz) δ 6.58 (m, 1, H4), 5.08 (m, 1, H3), 3.10 (m, 1, H2), 1.76 (m, 2, H1's), 1.32 (m, 18, PMe_3's), 1.01 (m, 9, PMe_3); $^{13}C\{^1H\}$ NMR (C_6D_6, 22 °C, 75 MHz) δ 157.7 (d, J_{H-P} = 13.4 Hz, C4), 108.8 (s, C3), 42.6 (d, J_{C-P} = 33.2 Hz, C2), 23.8 (d, J_{C-P} = 37.4 Hz, C1), 20.2 (m, PMe_3's), 19.2 (d, J_{C-P} = 37.2 Hz, PMe_3); $^{31}P\{^1H\}$ NMR (C_6D_6, 22 °C, 121 MHz, referenced to H_3PO_4) δ −41.1 (dd, J_{P-P} = 47.4, 10.6 Hz, 1), −44.3 (dd, J_{P-P} = 14.6, 10.6 Hz, 1), −47.7 (dd, J_{P-P} = 47.4, 14.6 Hz, 1).

(13) Synthesis of **4**: Under nitrogen, trimethylphosphine (0.26 g, 3.4 mmol) was added dropwise to a cold (−78 °C) stirred solution of $[(cyclooctene)_2Ir(Cl)]_2$ (0.50 g, 0.56 mmol) in THF. Potassium oxapentadienide (0.22 g, 2.0 mmol) in 10 mL of THF was then added dropwise. After the mixture was warmed to room temperature and stirred overnight (to allow conversion of **3** to **4**), the volatiles were removed under vacuum and the residue was extracted with pentane. Concentration of the pentane extract, followed by cooling to −30 °C, produced pure yellow crystals of **4**, yield 0.33 g, 60%. Anal. Calcd for $C_{13}H_{32}OIrP_3$: C, 31.89; H, 6.60. Found: C, 32.31; H, 6.81.

(14) Other examples of (η^3-oxapentadienyl)metal complexes have recently been reported by Liu et al.: (a) Cheng, M.-H.; Wu, Y.-J.; Wang, S.-L.; Liu, R.-S. *J. Organomet. Chem.* **1989**, *373*, 119. (b) Cheng, M.-H.; Cheng, C.-Y.; Wang, S.-L.; Peng, S.-M.; Liu, R.-S. *Organometallics* **1990**, *9*, 1853. See also: (c) Bannister, W. D.; Green, M.; Haszeldine, R. N. *J. Chem. Soc. A* **1966**, 194. (d) Green, M.; Hancock, R. I. *J. Chem. Soc. A* **1968**, 109. (e) White, C.; Thompson, S. J.; Maitlis, P. M. *J. Organomet. Chem.* **1977**, *134*, 319.

(15) The S-shaped anti configuration of the η^3-oxapentadienyl ligand, shown in Scheme II, has been confirmed by a preliminary X-ray diffraction study of the PMe_2Ph analogue of **4** (η^3-oxapentadienyl)$Ir(PMe_2Ph)_3$: Bleeke, J. R.; Haile, T.; Chiang, M. Y. To be submitted for publication.

The presence of the free (unbonded) formyl group is clearly indicated by the ^1H and $^{13}C\{^1H\}$ NMR spectra of 4,[16] which exhibit peaks at δ 7.46 and 173.75 for the formyl hydrogen and carbon, respectively. The infrared spectrum shows a characteristic C=O stretch at 1599 cm^{-1}. At room temperature, compound 4 undergoes a fluxional process that exchanges the three phosphine ligands, causing the $^{31}P\{^1H\}$ NMR signal to appear as a singlet at 25 °C. However, as the compound is cooled to −80 °C, the exchange process is stopped, and the $^{31}P\{^1H\}$ NMR spectrum decoalesces to three well-separated doublet of doublet patterns. This fluxional process probably involves $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ interconversions of the oxapentadienyl ligand.

When compound 4 is refluxed in acetone, it gradually (over a period of 24 h) undergoes metal-centered activation of the aldehydic (formyl) C–H bond to produce the iridacyclopentenone complex $(\overline{IrCH_2CH{=}CHC}{=}O)(PMe_3)_3(H)$ (**5**; Scheme III).[17,18] This conversion of **4** to **5** probably involves the 16e η^1-oxapentadienyl species (A, Scheme III) as the key intermediate. The X-ray crystal structure of **5**,[19] shown in Figure 2, exhibits an essentially planar five-membered ring (mean deviation of the ring atoms and oxygen 0.052 Å). The coordination geometry is octahedral, but unlike **2**, the phosphines adopt a *fac* arrangement. As a result, all three phosphines are inequivalent and give rise to three separate signals in the $^{31}P\{^1H\}$ NMR spectrum.[20] The hydride ligand resides trans to a phosphine ligand and exhibits a characteristically strong trans H–P coupling (J_{H-P} = 128.9 Hz).

In summary, we have demonstrated that metallaoxacyclohexadiene ("metallapyran") and metallacyclopentenone complexes can be synthesized via metal-centered activation of C–H bonds in (oxapentadienyl)metal precursors. The reaction chemistry of these novel metallacycles is currently under investigation in our laboratories and will be reported in a future communication.

Acknowledgment. We thank the National Science Foundation (Grants CHE-8520680 and CHE-9003159) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. A loan of $IrCl_3 \cdot 3H_2O$ from Johnson Matthey, Inc., 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 Research Support Instrument Grant 1 S10 RR02004 and by a gift from Monsanto Co.

Note Added in Proof. Recently, we have discovered that iridaoxacyclohexadiene complex **2** is converted to the iridacyclopentenone complex *fac*-$(\overline{IrCH_2CH{=}CHC}{=}O)(PEt_3)_3(H)$ upon stirring in benzene at 22 °C for 3 days.

Supplementary Material Available: Listings of final atomic coordinates, thermal parameters, bond lengths, and bond angles for **2** and **5** and an ORTEP drawing showing the positions of disordered atoms in **2** (9 pages); tables of observed and calculated structure factor amplitudes for **2** and **5** (39 pages). Ordering information is given on any current masthead page.

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(16) Spectroscopic data for **4** (carbon atoms in the chain are numbered by starting at the end opposite oxygen): ^1H NMR (C_6D_6, 22 °C, 300 MHz) δ 7.46 (d, J_{H-H} = 8.7 Hz, 1, H4), 4.32 (m, H2), 4.10 (m, H3), 1.16 (s, 28, PMe$_3$'s), 0.71 (m, 2, H1's); $^{13}C\{^1H\}$ NMR (C_6D_6, 22 °C, 75 MHz) δ 173.7 (s, C4), 62.2 (d, J_{C-P} = 2.7 Hz, C3), 53.1 (s, C2), 22.8 (filled-in d, J_{C-P} = 33.8 Hz, PMe$_3$'s), 17.3 (q, J_{C-P} = 8.3 Hz, C1); $^{31}P\{^1H\}$ NMR (C_6D_6, 22 °C, 121 MHz, referenced to H_3PO_4) δ −54.3 (s). At low temperature, this singlet decoalesces to three dd patterns: $^{31}P\{^1H\}$ NMR ($C(O)(CD_3)_2$, −80 °C, 121 MHz) δ −45.5 (dd, J_{P-P} = 43.9, 15.1 Hz, 1), −51.1 (dd, J_{P-P} = 23.1, 15.1 Hz, 1), −55.5 (dd, J_{P-P} = 43.9, 23.1 Hz, 1). IR (toluene, 22 °C): 1599 cm^{-1} (C=O stretch).

(17) Synthesis of **5**: An acetone solution of **4** (0.12 g, 0.24 mmol) was refluxed under nitrogen for 24 h. The solution was then cooled to room temperature, and the solvent was removed under vacuum. The resulting residue was extracted with pentane and filtered. The pentane extract was reduced in volume, treated with several drops of acetone, and cooled to −30 °C to produce very light yellow crystals of **5**, yield 0.096 g, 80%. Anal. Calcd for $C_{13}H_{32}IrOP_2$: C, 31.89; H, 6.60. Found: C, 32.04; H, 6.66.

(18) The conversion of **4** to **5** also occurs at room temperature in acetone solution, but *very slowly*.

(19) Crystal data for **5**: yellow prism, 0.20 × 0.34 × 0.58 mm; monoclinic, space group *Cc*, a = 16.165 (4) Å, b = 9.468 (3) Å, c = 13.990 (3) Å, β = 115.35 (2)°, V = 1935.0 (9) Å^3, Z = 4, d_{calcd} = 1.680 g/cm^3, μ = 71.10 cm^{-1}; Siemens R3m/V diffractometer, graphite-monochromated Mo Kα radiation, 22 °C, $\theta/2\theta$ scanning technique; 4440 unique reflections with $3.5 < 2\theta < 55°$ collected, 3726 reflections with $I > 3\sigma(I)$ used in refinement; semiempirical absorption correction (ψ scans); R = 4.58%, R_w = 5.64%, GOF = 1.54, data-to-parameter ratio 23.1:1. The location of the hydride ligand was inferred from the positions of the heavy atoms in the molecule. In Figure 2, it was placed at an idealized position with Ir–H = 1.75 Å and angle P2–Ir–H = 180°.

(20) Spectroscopic data for **5** (carbon atoms in the chain are numbered by starting at the end opposite oxygen): ^1H NMR (C_6D_6, 22 °C, 300 MHz) δ 7.36 (br m, 1, H2), 6.18 (s, 1, H3), 2.91 (br d, J = 19.8 Hz, 1, H1), 1.86 (br m, 1, H1), 1.48 (d, J_{H-P} = 8.3 Hz, 9, PMe$_3$), 1.07 (d, J_{H-P} = 7.1 Hz, 9, PMe$_3$), 0.99 (d, J_{H-P} = 7.9 Hz, 9, PMe$_3$), −11.19 (dt, J_{H-P} = 128.9, 19.1 Hz, 1, Ir–H); $^{13}C\{^1H\}$ NMR (C_6D_6, 22 °C, 75 MHz) δ 161.6 (d, J_{C-P} = 5.9 Hz, C2), 152.1 (d, J_{C-P} = 24.0 Hz, C3), 21.9 (overlapping d's, PMe$_3$'s), 17.6 (d, J_{C-P} = 23.2 Hz, PMe$_3$), 10.2 (dt, J_{C-P} = 65.5, 4.3 Hz, C1) (the quaternary carbon C4 was not observed); $^{31}P\{^1H\}$ NMR (C_6D_6, 22 °C, 121 MHz, referenced to H_3PO_4) δ −51.2 (m, 1), −55.1 (m, 1), −61.9 (m, 1).

$Co_2(CO)_8$-Catalyzed Reaction of Cyclic Ortho Esters with a Hydrosilane and Carbon Monoxide. Novel Method for Homologation of 1,2-, 1,3-, and 1,4-Diols

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Received August 6, 1990

Summary: In the presence of $Co_2(CO)_8$, the reaction of cyclic ortho esters with a hydrosilane and carbon monoxide resulted in the incorporation of carbon monoxide to give diols having one additional carbon atom. The reaction proceeded under mild reaction conditions (0–25 °C, 1 atm of CO).

Recently, we reported the $Co_2(CO)_8$-catalyzed reaction of epoxides with a hydrosilane and carbon monoxide giving disilyl ethers of 1,3-diol derivatives as a result of incorporation of carbon monoxide.[1] The catalytic reaction can be regarded as a new method for the conversion of 1,2-diols to 1,3-diols, since a 1,2-diol has the same oxidation level

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(1) (a) Murai, T.; Kato, S.; Murai, S.; Toki, T.; Suzuki, S.; Sonoda, N. *J. Am. Chem. Soc.* **1984**, *106*, 6093. (b) Murai, T.; Yasui, E.; Kato, S.; Hatayama, Y.; Suzuki, S.; Yamasaki, Y.; Sonoda, N., Kurosawa, H.; Kawasaki, Y.; Murai, S. *J. Am. Chem. Soc.* **1989**, *111*, 7938.

0276-7333/91/2310-0021$02.50/0