An alternative explanation of the lack of formation of the Cr-S-coordinated species is that the oxygen-coordinated complex, **4**, is both the kinetic and thermodynamic product of the Cr(III)/ADPαS reaction. Because the thermodynamically most stable form of $Cr(NH_3)_4(ADP\alpha S)$ also requires oxygen coordination at the α-P (**5**) the difference in the behavior of **4** and **6** cannot be directly attributed to differences in ligands, viz. H_2O vs. NH_3. In addition, since the X-ray structures of the analogous P^1,P^2-bidentate $Co(NH_3)_4PP$[15] and $Cr(NH_3)_4PP$ complexes are essentially identical,[16] it is unlikely that steric factors contribute to a large extent to the difference in behavior of the Cr(III) and Co(III) complexes. The preference for Co-S vs. Co-O coordination might instead derive from the nephelauxetic effect.

Acknowledgment. This investigation was supported by NIH Grant GM-28688, American Heart Grant-in-Aid 83918, and NIH Career Development Award (Grant ES-00111) to D. D.-M.

Registry No. **1**, 58642-43-6; Λ-**1**, 73037-58-8; Δ-**1**, 73000-97-2; **4**, 89791-44-6; Λ-**4**, 89885-94-9; Δ-**4**, 89885-95-0; **5**, 89791-45-7; Λ-**5**, 89885-96-1; Δ-**5**, 89885-97-2; **6**, 89791-46-8; Δ-**6a**, 89955-24-8; Λ-**6b**, 89908-10-1; Λ-**6c**, 89885-98-3; Δ-**6d**, 89885-99-4; $[Cr(H_2O)_4Cl_2]Cl$, 13820-85-4; $[Cr(NH_3)_4Cl_2]Cl$, 19706-96-8; $[Co(NH_3)_4CO_3]NO_3$, 15040-52-5.

---

(15) Merrit, E. A.; Sundaralingam, M. *Acta Crystallogr., Sect. B* **1980**, *B36*, 2576.

(16) Haromy, T.; Knight, W. B.; Dunaway-Mariano, D.; Sundaralingam, M. *Acta Crystallogr., Sect. B: Struct. Sci.*, in press.

Contribution from the Department of Chemistry,
University of Rochester, Rochester, New York 14627

Flexibly Bridged Binuclear Rhodium and Iridium Complexes of *p*-Xylylenebis(3-(2,4-pentanedione))

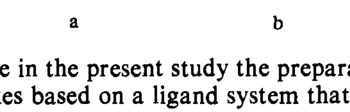
BRYAN C. WHITMORE and RICHARD EISENBERG*

Received September 30, 1983

Binuclear complexes of Rh and Ir containing a flexibly bridging bis(2,4-pentanedionato)ligand have been synthesized and characterized. The reaction of $[M(\mu\text{-Cl})(1,5\text{-COD})]_2$ (M = Rh, Ir) with *p*-xylylenebis(3-(2,4-pentanedione)), $xyl(Hacac)_2$, and 2 equiv of KOH results in the formation of the binuclear compounds $(M(COD))_2(xyl(acac)_2)$. The cyclooctadiene ligand in these complexes is readily displaced from the metal centers by either CO or PPh_3, leading to the formation of $(M(CO)_2)_2(xyl(acac)_2)$ and $(M(PPh_3)_2)_2(xyl(acac)_2)$, respectively. The $(M(CO)_2)_2(xyl(acac)_2)$ complexes react with excess triphenylphosphine, leading to the displacement of one CO from each metal center and the formation of $(M(CO)(PPh_3))_2(xyl(acac)_2)$. The rhodium complex $(Rh(CO)_2)_2(xyl(acac)_2)$ also reacts with triphenyl phosphite to produce the phosphite derivative, $(Rh(P(OPh)_3)_2)_2(xyl(acac)_2)$, which is found to act as a catalyst precursor for propylene hydrogenation. At 24 °C and under 320 torr of $H_2 + C_3H_6$ (2.5:1), propane forms at the rate of 8 mol of product (mol of catalyst)$^{-1}$ h^{-1} in the presence of a 7.4×10^{-4} M solution of the phosphite derivative in toluene. The binuclear iridium complex $(Ir(CO)(PPh_3))_2(xyl(acac)_2)$ undergoes oxidative-addition reactions with allyl bromide or benzyl bromide, producing the iridium(III) species $(IrR(CO)(PPh_3)Br)_2(xyl(acac)_2)$ where R = σ-allyl and benzyl, respectively. The mononuclear iridium complex $Ir(PPh_3)_2(acac)$ has also been synthesized and characterized. The reaction of this complex with H_2 results in the formation of $IrH_2(PPh_3)_2(acac)$, whereas the reaction of Ir(COD)(acac) with H_2 in the presence of 2 equiv of PPh_3 leads to the formation of *mer*- and *fac*-$IrH_3(PPh_3)_3$ as determined by ^1H NMR spectroscopy. The significance of these reactions in terms of the stability of rhodium and iridium acac complexes in catalytic systems is discussed.

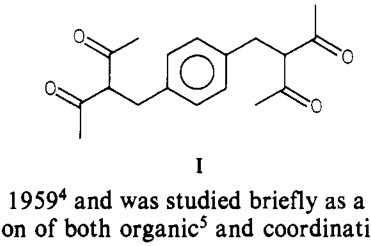
Introduction

Transition-metal complexes of β-diketonate ligands have been studied for many years because of the number and variety of stable complexes that they form and the spectroscopic and chemical properties that these complexes exhibit.[1,2] In these complexes, the six-membered chelate ring possesses a delocalized electronic structure, as suggested by resonance forms a and b, and exhibits partial aromatic character as evidenced by reaction chemistry of the acetylacetonate (acac) chelate ring.[3]



a b

We describe in the present study the preparation of binuclear complexes based on a ligand system that contains two acac moieties. The β-diketonate groups of the ligand system are connected by a xylylene bridge and are precluded from binding to a single metal center. The ligand, *p*-xylylenebis(3-(2,4-pentanedione))$(xyl(HAcac)_2)$, shown as I, was first prepared in 1959[4] and was studied briefly as a component in the formation of both organic[5] and coordination[6] polymers. We envisioned that this $(acac)_2$ compound would act as a flexible bridging ligand in the preparation of binuclear rhodium and iridium complexes, the mononuclear analogues of which have been studied extensively. Since 1964, when the rhodium complex $Rh(CO)_2(acac)$ and closely related derivatives were first reported,[7] many rhodium and iridium acac complexes have been studied and described in thee literature. Some of the Rh



I

---

(1) Mehrotra, R. C.; Bohra, R.; Gaur, D. P. "Metal β-Diketonates and Allied Derivatives"; Academic Press: New York, **1978**.

(2) Graddon, D. P. *Coord. Chem. Rev.* **1969** *4*, 1.

(3) Collman, J. P. *Angew. Chem.* **1965**, *77*, 154.

(4) Martin, D. F.; Fernelius, W. C.; Shamma, M. *J. Am. Chem. Soc.* **1959**, *81*, 130.

(5) Korshak, V. V.; Krongauz, E. S.; Berlin, A. M. *J. Polymer Sci., Part A* **1965**, *3*, 2425.

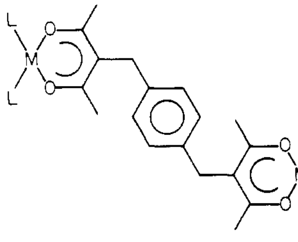
(6) Korshak, V. V.; Krongauz, E. S.; Sheina, V. E. *Vysokomol. Soedin.* **1960**, *2*, 662.

(7) Bonati, F.; Wilkinson, G. *J. Chem. Soc.* **1964**, 3156.

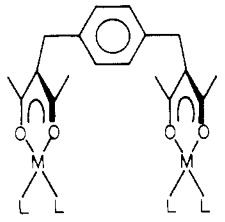
0020-1669/84/1323-1697$01.50/0 © 1984 American Chemical Society

systems have found use as catalyst precursors for hydrogenation[8] and hydroformylation[9] reactions.

The Rh and Ir binuclear complexes based on I belong to a group of flexibly bridged binuclear systems which, according to molecular models, possess metal centers separated by distances that vary from a minimum of 4 Å to a maximum of 12 Å. The flexibility of the binuclear systems results from rotational freedom about the $C_{phenyl}-C_{benzyl}$ bond of the xylylene unit. The conformation presumed to be most stable sterically has a trans arrangement of the complexed metal ions, as shown by A. However, the flexibility of the xyl(acac)$_2$ ligand allows a facile face-to-face approach of the transition-metal centers, B, thereby providing a site for substrate binding between the metal ions in an intramolecular fashion. Complexes of this type thus have the potential to serve as multielectron binuclear catalysts.



A



B

Experimental Section

All reactions were routinely performed under an N_2 atmosphere by using either modified Schlenk techniques or a Vacuum Atmospheres drybox. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Physical Measurements. ^1H and ^{31}P NMR spectra were recorded on a Bruker WH400 400-MHz instrument with chemical shifts reported in ppm relative to Me_4Si. Deuterated solvents were purchased from Aldrich, dried over sodium, and distilled in vacuo prior to use. Infrared spectra were recorded on a Perkin-Elmer Model 467 grating spectrophotometer. Samples were either KBr pellets or Nujol mulls on NaCl plates. Electronic spectra were recorded on a Perkin-Elmer Model 330 spectrophotometer. Extinction coefficients are given in M^{-1} cm^{-1}. Mass spectra were recorded on a Du Pont 490-B GC-MS mass spectrometer.

Reagents. All solvents used were analytical reagent grade except where otherwise noted. THF was distilled from sodium-lead alloy and benzophenone under N_2 prior to use. $[Rh(\mu\text{-}Cl)(1,5\text{-}COD)]_2$,[10] $[Ir(\mu\text{-}Cl)(1,5\text{-}COD)]_2$[11] and *p*-xylylenebis(3-(2,4-pentanedione))[4] were prepared by literature methods.

[*p*-Xylylenebis(3-(2,4-pentanedionato))]bis((cyclooctadiene)rhodium) (1). $Rh_2(COD)_2(\mu\text{-}Cl)_2$ (0.50 g, 1 mmol) and *p*-xylylenebis(3-(2,4-pentanedione)) (0.30 g, 1 mmol) are combined in degassed diethyl ether (10 mL) under a nitrogen atmosphere at −78 °C. Aqueous KOH (2 mL, 1 M) is then added dropwise over 10 min. The resulting solution is stirred under nitrogen at 0 °C for 45 min. Ether (5 mL) and water (10 mL) are then added to the reaction solution, the organic layer is separated, and the aqueous phase is extracted with 1:1 THF/diethyl ether (4 × 25 mL). The combined organic phase is then dried over $MgSO_4$, filtered, reduced in volume to 10 mL, and chilled. The resulting yellow precipitate is filtered and washed with ethanol. The filtrate volume is reduced by 50%, yielding additional product by precipitation; combined yield 0.50 g (69%). Anal. Calcd for $C_{34}H_{44}O_4Rh_2$: C, 56.52; H, 6.14. Found: C, 56.51; H, 6.39. IR (KBr): 1554, 1430, 1354, 1272, 1019, 950, 455 cm^{-1}. Mass spectrum (*m*/*e*): 722 (M^+), 679, 512, 470, 469 (base). ^1H NMR ($CDCl_3$): 7.03 (s, 4, aromatic), 4.05 (s, 8, vinyl), 3.60 (s, 4, benzylic), 2.41, 1.85 (multiplets, 16, methylene), 1.96 (s, 12 methyl).

[*p*-Xylylenebis(3-(2,4-pentanedionato))]bis(dicarbonylrhodium) (2). Carbon monoxide is passed through a stirred suspension of **1** (0.50 g, 0.69 mmol) in hexane (10 mL) for 30 min. The orange precipitate, **2**, is filtered, washed with hexanes (10 mL) and diethyl ether (15 mL), and dried in vacuo; yield 0.35 g (81%). Anal. Calcd for $C_{22}H_{20}O_8Rh_2$: C, 42.74; H, 3.28; O, 20.70. Found: C, 42.60; H, 3.43; O, 20.48. IR (KBr): 2070, 1970, 1563, 1450, 1370, 1289, 1172, 1023, 954, 527, 467 cm^{-1}. ^1H NMR (CD_2Cl_2): 7.01 (s, 4, aromatic), 3.70 (s, 4, benzylic), 2.09 (s, 12, methyl).

[*p*-Xylylenebis(3-(2,4-pentanedionato))]bis(carbonyl(triphenylphosphine)rhodium) (3). Triphenylphosphine (0.085 g, 0.32 mmol) is added to **2** (0.10 g, 0.16 mmol) in THF (5 mL) under N_2. The solution is stirred for 30 min and the solvent removed in vacuo. The solid residue is washed with diethyl ether (20 mL) and dried in vacuo; yield 0.17 g (98%). Anal. Calcd for $C_{54}H_{50}P_2O_6Rh_2$: C, 61.02; H, 4.75; P, 5.83; 0, 9.03. Found: C, 61.20; H, 4.66; P, 5.90; O, 8.84. IR (KBr): 1954, 1560, 1435, 1362, 1284, 1100, 951, 751, 698, 597, 531, 452 cm^{-1}. ^1H NMR (CD_2Cl_2): 7.30–7.80 (m, 30, aromatic), 7.00 (s, 4, aromatic), 3.62 (s, 4, benzyl), 2.10 (s, 6, methyl), 1.62 (s, 6, methyl).

[*p*-Xylylenebis(3-(2,4-pentanedionato))]bis(bis(triphenyl phosphite)rhodium) (4). To a suspension of **2** (0.021 g, 0.035 mmol) in degassed diethyl ether (5 mL) under N_2 is added triphenyl phosphite (46 mL, 0.175 mmol). The solution rapidly clears, and then formation of yellow needles occurs. The yellow solid is filtered in air, washed with diethyl ether (10 mL), and dried in vacuo; yield, 0.056 g (92%). Anal. Calcd for $C_{90}H_{80}O_{16}P_4Rh_2$: C, 61.86; H, 4.62; P, 7.09. Found: C, 60.32; H, 4.54; P, 6.99. IR (KBr): 1588, 1573, 1485, 1450, 1361, 1283, 1192, 1164, 1071, 1024, 936, 890, 760, 690, 603, 500 cm^{-1}. ^1H NMR (C_6D_6): 7.50 (d, 24, ortho $P(OPh)_3$)), 7.03 (dd, 24, meta ($P(OPh)_3$)), 6.86 (t, 12, para ($P(OPh)_3$)), 6.75 (s, 4, aromatic), 3.21 (s, 4, benzylic), 1.53 (s, 12, methyl).

[*p*-Xylylenebis(3-(2,4-pentanedionato))]bis(bis(triphenylphosphine)rhodium) (5). To complex **1** (0.032 g, 0.029 mmol) in degassed THF (5 mL) under nitrogen is added triphenylphosphine (0.10 g, 0.382 mmol) in THF (1 mL). The reaction mixture is stirred at room temperature for 2 h, the solvent is removed in vacuo, and diethyl ether (5 mL) is added. The solids are filtered, washed with diethyl ether (25 mL), and dried in vacuo; yield 0.041 g (91%). Anal. Calcd for $C_{90}H_{80}O_4P_4Rh_2$: C, 69.49; H, 5.19; P, 7.96. Found: C, 69.80; H, 4.97; P, 8.08. IR (KBr): 1557, 1483, 1436, 1363, 1280, 1190, 1123, 1098, 755, 727, 701, 543 cm^{-1}. ^1H NMR (C_6D_6): 7.85 (m, 24, aromatic), 6.93 (m, 40, aromatic), 3.50 (s, 4, benzylic), 1.53 (s, 12, methyl).

[*p*-Xylylenebis(3-(2,4-pentanedionato))]bis(carbonyl(triethylphosphine)rhodium) (6). Triethylphosphine (5.6 μL, 0.038 mmol) and CD_2Cl_2 (0.5 mL) are distilled in vacuo into a 5-mm NMR tube containing **2** (0.0117 g, 0.019 mmol), and the tube is sealed in vacuo. The reaction product is identified by ^1H NMR spectroscopy only. ^1H NMR (CD_2Cl_2): 7.04 (s, 4, aromatic), 3.67 (s, 4, benzylic), 2.07 (s, 6, methyl), 1.92 (s, 6, methyl), 1.82 (dq, 12, $P(CH_2CH_3)_3$, J_{PH} = 7.8 Hz), 1.19 (dt, 18, $P(CH_2CH_3)_3$, J_{PH} = 16.6 Hz).

[*p*-Xylylenebis(3-(2,4-pentanedionato))](bis(diphenylphosphino)propane)bis(carbonylrhodium) (7). Bis(diphenylphosphino)propane (0.233 g, 0.57 mmol) in THF (50 mL) is added over a 30-min period to a THF solution (50 mL) of **2** (0.350 g, 0.57 mmol) under N_2. The reaction mixture is stirred an additional 45 min and the solvent volume reduced to 50 mL in vacuo. Degassed diethyl ether (50 mL) is added, and the yellow precipitate is filtered, washed with ether, and dried in vacuo; yield 0.45 g (81%). Anal. Calcd for $C_{47}H_{46}P_2O_6Rh_2$: C, 57.91; H, 4.77; P, 6.35. Found: C, 57.60; H, 4.68; P, 5.93. IR (Nujol): 1965, 1562, 1436, 1280, 1164, 1101, 1020, 950, 746, 700 cm^{-1}. ^1H NMR (C_6D_6): 7.71 (m, 8, ortho (PPh_2)), 7.02 (m, 12, meta, para (PPh_2)), 6.82 (s, 4, aromatic), 3.41 (s, 4, benzylic), 2.64 (dt, 4, $CH_2(CH_2PPh_2)_2$), 2.17 (m, 2, $CH_2(CH_2PPh_2)_2$), 2.03 (s, 6, methyl), 1.62 (s, 6, methyl). $^{31}P\{H\}$ NMR (30% C_6D_6/C_6H_6): 43.78 (d, J_{Rh-P} = 172.7 Hz). M_r: calcd for x = 1, 975; calcd for x = 2, 1950; found (THF), 1552 (determined by vapor pressure osmometry, Galbraith Laboratories).

Molecular-Exclusion Chromatography. Bio-Beads SX4 were placed in CH_2Cl_2 and packed into a 50-mL buret using CH_2Cl_2 as the eluant, yielding a 13 in. × 1/2 in. column. Six rhodium and iridium complexes were then used to obtain a calibration curve for molecular weight. The complexes (10 mg) were dissolved in 0.5 mL of CH_2Cl_2, loaded onto the column, and eluted with CH_2Cl_2. The time of elution for each complex was measured and plotted against log M_r as shown in

---

(8) (a) Pieta, D.; Trzeciak, A. M.; Ziółkowski, J. J. *J. Mol. Catal.* **1983**, *18*, 193. (b) Shebaldova, A. D.; Bystrening, V. I.; Kravtsova, V. N.; Khidekel, M. L. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1975**, 2101.

(9) (a) King, R. B.; King, A. D., Jr.; Iqbal, M. Z. *J. Am. Chem. Soc.* **1979**, *101*, 4893. (b) Hartley, F. R.; Murray, S. G.; Nicholson, P. N. *J. Mol. Catal.* **1982**, *16*, 363.

(10) Chatt, J.; Venanzi, L. M. *J. Chem. Soc.* **1957**, 4735.

(11) Herde, J. L.; Lambert, J. C.; Senott, C. V. *Inorg. Synth.* **1974**, *15*, 18.

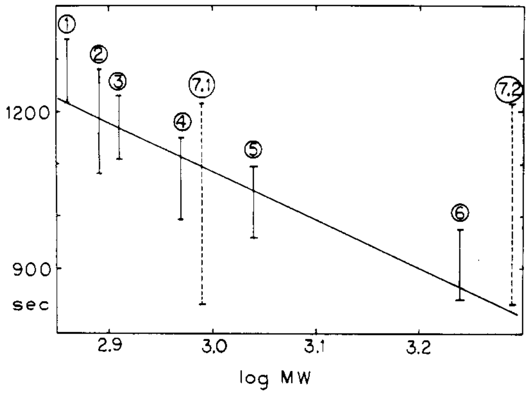


Figure 1. Plot of log (MW) (log M_r) vs. elution time for a series of known complexes and for complex **7**. Numbers refer to compounds given in Table I.

Table I. Molecular-Exclusion Chromatography Data

fraction	complex	mol wt (M_r)	log M_r	elution time, s
1	$[Rh(COD)]_2(xyl(acac)_2)$	722	2.86	1215–1335
2	$IrCl(CO)(PPh_3)_2$	779	2.89	1080–1280
3	$Rh(P(OPh)_3)_2(acac)$	822	2.91	1110–1230
4	$RhCl(PPh_3)_3$	924	2.97	990–1150
5	$Rh_2Cl_2(CO)_2(dpm)_2$	1101	3.04	960–1095
6	$[Rh(P(OPh)_3)_2]_2(xyl(acac)_2)$	1746	3.24	835–975

Figure 1. Complex **7** was then treated in a similar fashion. Band 7.1 is given with complex **7** formulated as a monomer (M_r = 975) while band 7.2 is given with a dimer formulation (M_r = 1950). The complexes used as standards and their molecular weights and retention times are given in Table I.

Hydrogenation of C_3H_6 with $(Rh(P(OPh)_3)_2)_2(xyl(acac)_2)$ (4). A 500-mL flask containing complex **4** (12.9 mg, 7.4 μmol) in toluene (10 mL) is charged with propylene (92 torr) and H_2 (228 torr). The reaction mixture is stirred at room temperature (24 °C), and the gas phase is examined periodically by gas chromatography using a 12 m × $^1/_4$ in. Poropack Q on Chromasorb P column.

[*p*-Xylylenebis(3-(2,4-pentanedionato))]bis((cyclooctadiene)iridium) (8). $[Ir(\mu\text{-}Cl)(1,5\text{-}COD)]_2$ (0.60 g, 0.89 mmol) and *p*-xylylenebis(3-(2,4-pentanedione)) (0.27 g, 0.89 mmol) are combined under N_2 in degassed diethyl ether (10 mL), and aqueous KOH (2.5 mL, 1 M) is then added. The solution is stirred for 30 min, water is added (20 mL), and the ether is removed in vacuo. The yellow solid is filtered in air, washed with 2-propanol (20 mL), pentane (20 mL), and diethyl ether (10 mL), and dried in vacuo; yield 0.58 g (72%). Anal. Calcd for $C_{34}H_{44}O_4Ir_2$: C, 45.31; H, 4.93; O, 7.10. Found: C, 44.90; H, 5.02; O, 7.17. IR (KBr): 1545, 1446, 1347, 1280, 1160, 1005, 980, 954, 914, 756, 639, 464 cm^{-1}. ^{1}H NMR (CD_2Cl_2): 7.04 (s, 4, aromatic), 3.91 (s, 8, vinylic), 3.72 (s, 4, benzylic), 2.21, 1.64 (m, 16, methylene), 2.03 (s, 12, methyl).

[*p*-Xylylenebis(3-(2,4-pentanedionato))]bis(dicarbonyliridium) (9). CO gas is passed through a stirred suspension of **8** (0.126 g, 0.14 mmol) in hexane (20 mL) for 30 min. The purple solid is filtered, washed with diethyl ether (25 mL), and dried in vacuo; yield 0.11 g (99%). Anal. Calcd for $C_{22}H_{20}O_8Ir_2$: C, 33.16; H, 2.53; O, 16.06. Found: C, 32.65; H, 2.52, O, 16.11. IR (KBr): 2051, 1965, 1554, 1455, 1335, 1291, 1170, 955 cm^{-1}. ^{1}H NMR (C_6D_6): 6.67 (s, 4, aromatic), 3.17 (s, 4, benzylic), 1.66 (s, 12, methyl). UV–vis (C_6H_6), λ_{max} nm (ϵ): 375 (2400), 330 (12 500), 310 (15 400).

[p-Xylylenebis(3-(2,4-pentanedionato))]bis(carbonyl(triphenylphosphine)iridium) (10). Triphenylphosphine (0.026 g, 0.10 mmol) in THF (10 mL) is added to **9** (0.040 g, 0.05 mmol) under nitrogen, and the mixture is stirred at room temperature for 1 h. Degassed pentane (20 mL) is added, and the yellow precipitate is filtered and washed with diethyl ether (10 mL); yield 0.055 g (87%). Anal. Calcd for $C_{56}H_{50}P_2O_6Ir_6$: C, 53.15; H, 3.99; P, 4.89. Found: C, 54.00; H, 4.08; P, 5.20. IR (KBr): 1950, 1554, 1455, 1433, 1350, 1287, 1099, 750, 696, 546 cm^{-1}. ^{1}H NMR (C_6D_6): 7.87 (m, 12, aromatic), 7.01 (m, 18, aromatic), 6.76 (s, 4, aromatic), 3.34 (s, 4, benzylic), 1.87 (s, 6, methyl), 1.41 (s, 6, methyl).

[*p*-Xylylenebis(3-(2,4-pentanedionato))]bis(bis(triphenylphosphine)iridium) (11). To **8** (0.15 g, 0.17 mmol) under nitrogen is added triphenylphosphine (0.175 g, 0.67 mmol) dissolved in degassed THF (10 mL). The reaction mixture is refluxed for 4 h and then treated with degassed hexanes (10 mL). The solution is cooled to room temperature and filtered under nitrogen, and the resulting precipitate is washed with diethyl ether (5 mL); yield 0.27 g (92%). Anal. Calcd for $C_{90}H_{80}O_4P_4IR_2$: C, 62.34; H, 4.66; P, 7.14. Found: C, 61.96; H, 4.54; P, 7.10. IR (KBr): 1551, 1432, 1362, 1284, 1092, 745, 695, 564, 533 cm^{-1}. ^{1}H NMR (C_6D_6): 7.88 (m, 24, aromatic), 6.93 (m, 36, aromatic), 6.79 (s, 4, aromatic), 3.44 (s, 4, benzylic), 1.32 (s, 12, methyl).

[*p*-Xylylenebis(3-(2,4-pentanedionato))]bis((σ-allyl)carbonylbromo(triphenylphosphine)iridium) (12). Triphenylphosphine (0.37 g, 0.14 mmol) in THF (6 mL) is added to **9** (0.056 g, 0.07 mmol) under N_2, and the solution is refluxed for 10 min. Allyl bromide (12 μL, 0.14 mmol) is then added, and the reaction mixture is refluxed for 12 h. The solution is cooled to room temperature, and degassed hexane (10 mL) is then added. The tan solid is filtered, washed with hexanes (10 mL), and dried in vacuo; yield 0.09 g (93%). Anal. Calcd for $C_{62}H_{60}O_6P_2Br_2Ir_2$: C, 49.40; H, 3.98. Found: C, 49.81; H, 4.10. IR (KBr): 2038, 1568, 1453, 1435, 1316, 1283, 1099, 750, 698, 546, 520 cm^{-1}. ^{1}H NMR (C_6D_6): 7.90 (m, 12, aromatic), 6.9–7.1 (m, 22, aromatic), 6.17 (m, 2, vinyl), 4.94 (m, 4, vinyl), 3.41 (s, 4, benzyl), 2.91 (m, 2, IR–C*H*H′), 2.58 (m, 2, Ir–CH*H*′), 1.94 (s, 6, methyl), 1.65 (s, 6, methyl).

[*p*-Xylylenebis(3-(2,4-pentanedionato))]bis(benzylbromocarbonyl(triphenylphosphine)iridium) (13). Triphenylphosphine (0.0678 g, 0.26 mmol) and **9** (0.103 g, 0.13 mmol) are combined in THF (20 mL) under N_2. Benzyl bromide (31 μL, 0.26 mmol) is added to the reaction solution, which is then refluxed 3 h. The solvent is removed in vacuo, diethyl ether (10 mL) is added, and the tan solid is filtered and dried in vacuo. The complex is characterized by IR and ^{1}H NMR spectroscopy. IR (KBr): 2034, 1569, 1451, 1436, 1360, 1282, 1095, 750, 698, 547, 532 cm^{-1}. ^{1}H NMR (C_6D_6): 7.94 (m, 12, σ aromatic (PPh_3)), 6.9–7.4 (multiplets, remaining aromatics + C_6H_6), 3.48 (dd, 2, Ir–C*H*H′), 3.39 (s, 4, benzylic), 2.96 (dd, 2, Ir–CH*H*′), 1.64 (s, 6, CH_3), 1.63 (s, 6, CH_3).

Ir(1,5-COD)(acac) (14). This complex was not prepared by the literature method[12] but by a modification of the procedure used to prepare **8**, using acetylacetone in place of xyl(Hacac)$_2$; yield 81%. The complex gave satisfactory IR and ^{1}H NMR spectra.

$Ir(CO)_2(acac)$ (15). Similarly, this complex was not prepared by the literature method[13] but by passing CO through a hexane suspension of Ir(COD)(acac); yield 94%. UV–vis (C_6H_6), λ_{max} nm (ϵ): 375 sh (560), 338 (2550), 300 (5140). The complex gave satisfactory IR and ^{1}H NMR spectra.

$Ir(PPh_3)_2(acac)$ (16). Triphenylphosphine (0.283 g, 1.08 mmol) dissolved in THF (10 mL) is added to Ir(COD)(acac) (0.21 g, 0.536 mmol) under nitrogen. The solution is refluxed for 3 h cooled to room temperature, treated with hexanes (30 mL), and allowed to stand overnight. The resulting yellow crystals are then filtered and washed with diethyl ether (5 mL); yield 0.39 g (90%). Anal. Calcd for $C_{41}H_{37}O_2P_2Ir$: C, 60.35; H, 4.58; P, 7.59. Found: C, 60.51; H, 4.41; P, 7.43. IR (KBr): 1561, 1516, 1476, 1431, 1392, 1273, 1182, 1092, 1027, 735, 698, 564, 528 cm^{-1}. ^{1}H NMR (C_6D_6): 7.84 (m, 12, aromatic), 6.92 (m, 18, aromatic), 5.31 (s, 1, central-C*H*, acac), 1.29 (s, 6, methyl).

(σ-Allyl)bromocarbonyl(2,4-pentanedionato)(triphenylphosphine)iridium (17). Triphenylphosphine (0.0153 g, 0.0584 mmol) in degassed benzene (10 mL) is added to $Ir(CO)_2(acac)$ under nitrogen, and the resulting solution is refluxed for 10 min. The mixture is cooled to room temperature, treated with allyl bromide (10 μL, 0.116 mmol), and stirred for 18 h. The solvent is removed in vacuo, and the solid is recrystallized from acetone/2-propanol. The complex is identified by IR and ^{1}H NMR spectroscopy. IR (Nujol): 2040, 1568, 1520, 1433, 1280, 1190, 1096, 752, 696 cm^{-1}. ^{1}H NMR (C_6D_6): 7.90 (m, 6, aromatic), 7.0 (m, 9, aromatic), 6.1 (m, 1, $=$C*H*CH_2), 5.2 (s, 1, *H*C$(COCH_3)_2$), 4.9 (m, 2, $=CH_2$), 2.85 (ddd, 1, CH—Ir), 2.45 (dd, ^{1}, CH′-Ir), 1.80 (s, 3, methyl), 1.50 (s, 3, methyl).

Reaction of $Ir(PPh_3)_2(acac)$ with H_2. Benzene-d_6 (0.5 mL) is distilled in vacuo into a 5-mm ^{1}H NMR tube containing complex **16** (2 mg). The tube is sealed under H_2 (440 torr) and heated to 70 °C. The reaction is monitored periodically by ^{1}H NMR spectroscopy. The

---

(12) Robinson, S. D.; Shaw, B. L. *Tetrahedron Lett.* **1964**, 1301.

(13) Bonati, F.; Ugo, R. *J. Organomet. Chem.* **1968**, *11*, 341.

hydrogenation is shown to be complete after 2 days by comparison of its ^{1}H NMR spectrum with literature values. ^{1}H NMR (C_6D_6): 7.99 (m, 12, ortho), 7.05 (m, 18, meta, para); 4.65 (s, 1, methine), 1.34 (s, 6, methyl), -24.75 (t, 2, Ir-H).

Reaction of Ir(COD)(acac) with H_2 and PPh_3. C_6D_6 (0.5 mL) is distilled in vacuo into a 5-mm ^{1}H NMR tube containing Ir(COD)(acac) (2.2 mg, 5.5 μmol) and PPh_3 (3.2 mg, 12 μmol), and the tube is sealed under H_2 (600 torr). The reaction is monitored by ^{1}H NMR spectroscopy (see Results and Discussion for more detailed analysis).

Reaction of $(Ir(COD))_2(xyl(acac)_2)$ with PPh_3 and H_2. Hydrogen is passed through an acetone solution (10 mL) of **8** (0.53 g, 0.059 mmol) and PPh_3 (0.062 g, 0.236 mmol) for 10 min. The tan precipitate is filtered, washed with pentane (10 mL), and dried in vacuo, yielding a mixture of iridium hydride complexes. *fac*-$IrH_3(PPh_3)_3$ selectively crystallizes from a Me_2SO-d_6 solution of the tan solid as white needles. ^{1}H NMR (C_6D_6): 7.39 (m, 18, ortho (PPh_3)), 6.81 (m, 27, meta, para (PPh_3)), -11.45 ppm (m, 3, IrH) (see Results and Discussion for more detailed analysis).

Results and Discussion

As we anticipated at the outset of this study, the $xyl(acac)_2^{2-}$ ligand readily forms binuclear Rh and Ir complexes for which the mononuclear mono(2,4-pentanedionato) analogues are known. The method of preparation involves substitution of the monoanionic acac moieties of I for chloride in the μ-Cl dimers of Rh(I) and Ir(I), followed by substitution reactions of the remaining neutral ligands. The results obtained including subsequent reaction chemistry of the Rh(I) and Ir(I) binuclear complexes of $xyl(acac)_2$ are now discussed in detail.

Rhodium Complexes. The dimer $[Rh(\mu\text{-}Cl)(1,5\text{-}COD)]_2$ reacts with I and 2 equiv of base to produce the binuclear Rh(I) cyclooctadiene complex, **1**, which is isolated as an air-stable yellow solid. Its IR spectrum shows a strong band at 1560 cm^{-1}, assignable to a bidentate β-diketonate group. The absence of bands near 1700 cm^{-1} indicates both β-diketonate moieties are coordinated to metal centers, producing a binuclear complex. The mass spectrum of **1** exhibits the molecular ion (M^+) at *m/e* 722. Other fragments observed include the $[M^+ - [\cdot C_2H_3O]]$ ion and a base peak attributable to $[M^+ - [\cdot C_2H_3] - [\cdot Rh(1,5\text{-}COD)]]$. The 400-MHz ^{1}H NMR spectrum of **1** further confirms its binuclear structure (see Table I). A singlet due to the equivalent aromatic protons of the binucleating ligand appears at 7.03 ppm while the benzylic and methyl protons appear as singlets at 3.60 and 1.96 ppm, respectively. The coordinated cyclooctadiene has resonances at 4.05, 2.41, and 1.85 ppm which can be assigned to the vinyl protons and the nonequivalent methylene protons.

The chelating diolefin ligand, 1,5-COD, is easily displaced by either CO or PPh_3. Thus the reaction of **1** with CO in a hexane suspension results in the isolation of the orange air-stable rhodium carbonyl complex, **2**. Its IR spectrum contains two strong bands at 2070 and 1970 cm^{-1}, assignable to the symmetric and antisymmetric stretches of the cis carbonyl ligands. A strong band at 1560 cm^{-1} shows that the β-diketone has remained chelated to the rhodium center. The loss of cyclooctadiene is confirmed by the ^{1}H NMR spectrum of **2**, which consists of three singlets at 7.01, 3.70, and 2.09 ppm assignable to the aromatic, benzylic, and methyl protons, respectively, of the $xyl(acac)_2$ ligand. Refluxing benzene solutions of complex **2** show no reaction with either H_2 or CH_3I, but complex **2** does react with HCl, causing the protonation and loss of the bridging ligand and the formation of $[Rh(\mu\text{-}Cl)(CO)_2]_2$. The same ligand displacement is observed for the mononuclear complex $Rh(CO)(PPh_3)(acac)$.[14]

The reaction of the binuclear rhodium cyclooctadiene complex, **1**, with triphenyl phosphine results in the displacement of the diolefin ligand and the formation of the bis(phosphine) complex, **5**. This complex is slightly air sensitive, gradually decomposing over several hours, in solution. Its IR spectrum verifies the presence of the chelated β-diketonate ($\nu_{acac} = 1557$ cm^{-1}), and its ^{1}H NMR spectrum shows the loss of cyclooctadiene resonances and the coordination of triphenylphosphine. The aromatic region contains resonances due to coordinated PPh_3 and the aromatic hydrogens from the bridging $xyl(acac)_2$ ligand. The benzylic protons appear as a singlet at 3.5 ppm and methyl protons are present at 1.53 ppm also as a singlet.

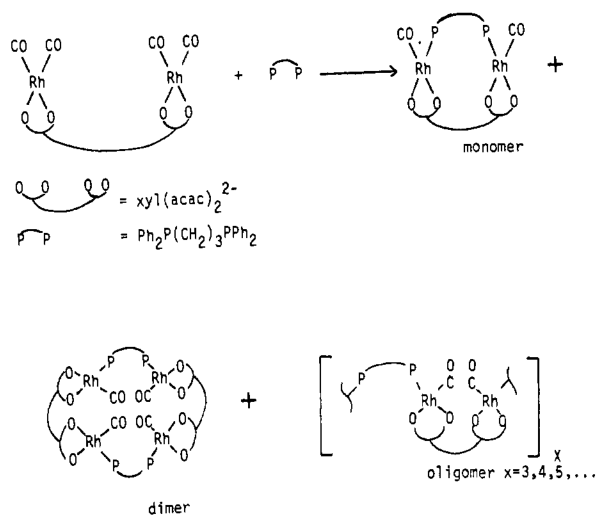
Displacement of CO. The dicarbonyl complex **2** reacts readily with excess triphenylphosphine, causing the displacement of one CO from each metal center and yielding the mixed phosphine carbonyl complex, **3**. A similar reaction occurs with $Rh(CO)_2(acac)$.[7] The IR spectrum of **3** contains one carbonyl stretch at 1950 cm^{-1}, indicating the loss of only one carbonyl from each rhodium center. A band at 1550 cm^{-1} confirms the presence of the chelated β-diketone group. The ^{1}H NMR spectrum of **3** shows the presence of one coordinated PPh_3 per metal center and contains a singlet at 7.00 ppm assignable to the aromatic protons on the bridging ligand. The methyl groups are no longer equivalent due to the loss of symmetry at the Rh(I) center and appear as singlets at 2.10 and 1.62 ppm. The benzylic protons are not affected by this loss of symmetry and remains as a singlet at 3.62 ppm. The rhodium dicarbonyl complex, **2**, also reacts with triethylphosphine to produce the carbonyl phosphine complex, **6**, as identified by its ^{1}H spectrum.

Since the reaction of the dicarbonyl complex, **2**, with phosphines results in the displacement of a single CO ligand from each rhodium center, we envisioned the addition of a second bridging moiety between the metal centers via the reaction of **2** with bis(phosphine) ligands. Thus, the reaction of bis(diphenylphosphino)propane with $[Rh(CO)_2]_2(xyl(acac)_2)$ in THF occurs as expected, resulting in the formation of the rhodium phosphine carbonyl complex, **7**. The IR spectrum of complex **7** contains a single band in the 1900–2100 cm^{-1} region indicating the presence of a single carbonyl ligand on each metal center. The β-diketonate ligand remains bound in a bidentate fashion as shown by the absence of bands near 1700 cm^{-1}. Both phosphines of the bis(phosphine) ligand are coordinated to equivalent rhodium centers as indicated by the presence of a doublet ($J = 172.7$ Hz) at 43.78 ppm in the $^{31}P\{^1H\}$ NMR spectrum of **7**. No free phosphine is detected by ^{31}P NMR spectroscopy. The mononuclear rhodium complex, $Rh(CO)(PPh_3)(acac)$, exhibits a resonance at 48.7 ppm ($CHCl_3$ solution, $J_{Rh-P} = 175.4$ Hz) in its ^{31}P NMR spectrum.[3] The elemental analysis and ^{1}H NMR spectrum of complex **7** are consistent with the reaction of 1 equiv of bis(phosphine) ligand with 1 equiv of binuclear rhodium complex, **2**. The ^{1}H NMR spectrum of **7** contains resonances in the aromatic region due to the phenyl groups of the phosphine ligand and due to the phenylene group of the bis(β-diketonate) moiety. The inequivalent methyl groups of $xyl(acac)_2$ yield resonances at 2.03 and 1.62 ppm, while the benzylic protons appear at 3.41 ppm, similar to the corresponding resonances observed for $[Rh(CO)(PPh_3)]_2(xyl(acac)_2)$. The propylene bridge of the bis(phosphine) ligand gives rise to two multiplets. The methylene hydrogens adjacent to phosphorus appear at 2.64 ppm while the central methylene hydrogens produce a multiplet at 2.17 ppm.

Several products are possible in this reaction, as shown in eq 1. They range from a 1:1 monomer that contains an intramolecularly bridging bis(phosphine) ligand to oligomers that contain intermolecular phosphine bridges. Entropy favors the formation of the intramolecularly bridged monomer as long as the binucleating $xyl(acac)_2^{2-}$ framework is flexible enough to allow a face-to-face approach of the rhodium centers.

---

(14) Barlex, D. M.; Hacker, M. J.; Kemmitt, R. D. W. *J. Organomet. Chem.* **1972**, *43*, 425.



(1)

Molecular weight measurement of complex **7** in THF yields an average molecular weight of 1552. This value is intermediate between that for a monomer (M_r = 975) and that for a dimer (M_r = 1950) and indicates that a portion of complex **7** is monomeric. Analysis of this reaction product by molecular-exclusion chromatography gives results as shown in Figure 1 and Table I. By comparison of the relative retention times of known molecular weight standards with that of complex **7** it is apparent that some monomer is present in the complex mixture. The broadness of the band indicates that some dimer is present also. These results suggest that there exists enough conformational flexibility in the xyl(acac)$_2$ framework to allow a face-to-face approach of the metal centers, which may then be locked by the binding of a bridging bis(phosphine) ligand. Attempts to isolate in crystalline form a pure sample of the monomeric intramolecularly bridged bis(phosphine) species are now in progress.

While the reaction of the rhodium dicarbonyl complex, **2**, with phosphines leads to a mixed carbonyl phosphine complex, the reaction of **2** with triphenyl phosphite results in complete displacement of the CO ligands, yielding the binuclear tetrakis(phosphite) complex **4**. This reaction parallels that demonstrated for the mononuclear complex, $Rh(CO)_2(acac)$.[15] The phosphite complex, **4**, prepared in 92% yield from the dicarbonyl complex **2** is isolated as a yellow, crystalline solid. The IR spectrum of **4** exhibits no bands in the region 1800–2200 cm^{-1}, indicating complete loss of CO from the rhodium center. The β-diketonate groups remain chelated as shown by the band at 1573 cm^{-1} and the absence of bands near 1700 cm^{-1}. The ^{1}H NMR spectrum of **4** contains the following resonances. The aromatic protons of the phosphite ligand, $P(OPh)_3$, are completely resolved and appear as multiplets at 7.50, 7.03, and 6.86 ppm assignable to the ortho, meta, and para protons, respectively. A singlet at 6.75 ppm is due to the aromatic protons of the xyl(acac)$_2$ ligand. The benzylic hydrogens give rise to a singlet at 3.21 ppm, and the equivalent methyl groups produce a singlet at 1.53 ppm. The mononuclear complex $Rh(P(OPh)_3)_2(acac)$ is an air-stable solid but the binuclear complex, **4**, decomposes in the solid state, gradually becoming dark brown over a period of several weeks.

The complex $Rh(P(OPh)_3)_2(acac)$ is reported to be a homogeneous catalyst precursor for the hydrogenation of aromatic hydrocarbons.[8a] We, therefore, examined briefly the activity of complex **4** as a catalyst precursor in the hydrogenation of simple olefins. Preliminary work indicates that **4** promotes the hydrogenation of propylene to propane. The rate of hydrogenation at 24 °C under 320 torr of $H_2 + C_3H_6$ (2.5:1) is 8 mol of propane (mol of **4**)$^{-1}$ h^{-1}. However, the catalyst solution exhibits signs of decomposition after 24 h of reaction.

Further investigations regarding the nature of the catalytically active species indicate that with both the mononuclear and binuclear complexes, $Rh(P(OPh)_3)_2(acac)$ and $(Rh(P(OPh_3)_2)_2(xyl(acac)_2)$, respectively, the integrity of the Rh(acac) unit is not maintained during catalysis. Thus, complex **4** serves simply as a catalyst precursor in the hydrogenation of propylene, yielding mononuclear, catalytically active species. Details regarding the $Rh(P(OPh)_3)_2(acac)$ system will be described elsewhere.[16]

Iridium Complexes. The same synthetic procedures used to make the rhodium complexes are used to prepare the iridium systems. In general, the iridium complexes are more air sensitive than their rhodium analogues. The binuclear iridium cyclooctadiene complex **8** is prepared from xyl(acac)$_2^{2-}$, generated in situ from I + KOH, and $[Ir(\mu\text{-}Cl)(1,5\text{-}COD)]_2$. This compound decomposes in air within several hours in solution but is air stable in the solid state. Its IR spectrum contains a band at 1545 cm^{-1} typical of a chelated β-diketonate. Its ^{1}H NMR spectrum is nearly identical with that of the binuclear rhodium complex **1**, with only minor differences in chemical shifts (see Table II).

The iridium complex undergoes the same basic reaction chemistry as its rhodium counterpart, and as its mononuclear analogue IR(1,5-COD)(acac), with cyclooctadiene being easily displaced by either carbon monoxide or triphenylphosphine, producing complexes **9** and **11**, respectively. The iridium carbonyl complex, **9**, is an air-stable purple solid, prepared by passing CO through a hexane suspension of the COD complex **8**. Its IR spectrum exhibits two carbonyl stretches at 2051 and 1965 cm^{-1} and a β-diketonate bond at 1554 cm^{-1}. Its ^{1}H NMR spectrum contains three singlets similar to the spectrum of complex **2**. Refluxing benzene solutions of the iridium carbonyl complex, **9**, exhibit no reaction with H_2 or CH_3I.

Displacement of CO. The iridium carbonyl complex, **9**, reacts with phosphines, resulting in the loss of only one carbonyl ligand from each metal center to give mixed carbonyl phosphine species. Thus **9** reacts with triphenylphosphine to give complex **10** as identified by its IR and ^{1}H NMR spectra. The IR spectrum contains a single carbonyl stretch at 1950 cm^{-1} and a band at 1554 cm^{-1} due to the chelated β-diketonate group. While the rhodium phosphine carbonyl complex, **3**, is fairly unreactive, the analogous iridium complex, **10**, is easily oxidized in solution and decomposes in $CHCl_3$. It also undergoes oxidative-addition reactions, yielding iridium(III) complexes.

Oxidative Additions. Whereas the binuclear rhodium complex **3** was found to be inert toward the oxidative addition of MeI or BzBr, the analogous iridium complex, **10**, easily undergoes oxidative additions. Thus, the reaction of **9** with allyl bromide results in the formation of a σ-bonded allyl complex, **12**, as identified by its IR and ^{1}H NMR spectra. In the carbonyl region of the IR spectrum we observe one band at 2038 cm^{-1}. The shift of 88 cm^{-1} from ν_{CO} in **10** to higher frequency indicates the oxidation of the Ir(I) to Ir(III) with concomitant decrease in the back-bonding to the carbonyl ligand.[17] The β-diketonate group remains chelated, as indicated by a strong band at 1568 cm^{-1} and the absence of bands in the region near 1700 cm^{-1}. The 400-MHz ^{1}H NMR spectrum contains the following resonances. The σ-bonded allyl gives rise to a multiplet at 5.93 ppm due to the central vinyl proton, overlapping resonances at 4.95 ppm assignable to the terminal vinyl protons, and multiplets at 2.91 and 2.57 ppm assignable to nonequivalent methylene resonances for the

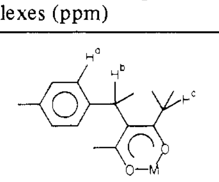
---

(15) Trzeciak, A. M.; Ziółkowski, J. J. *Inorg. Chim. Acta* **1982**, *64*, L267.

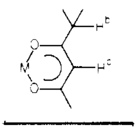
(16) Whitmore, B. C.; Eisenberg, R. *J. Am. Chem. Soc.*, in press.

(17) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 3rd ed.; Interscience: New York, 1972; p 687.

Table II. ^{1}H NMR Spectral Data for Binuclear and Mononuclear Complexes (ppm)



complex	H^a	H^b	H^c	others
1	7.03	3.60	1.96	COD: 4.05 (vinyl); 2.41, 1.85 (methylene)
2	7.01	3.70	2.09	
3	7.00	3.62	2.10, 1.62	PPh$_3$: 7.80 (ortho); 7.30 (meta, para)
4	6.75	3.21	1.53	P(OPh)$_3$: 7.50 (ortho); 7.03 (meta); 6.86 (para)
5	6.93	3.50	1.53	PPh$_3$: 7.85 (ortho); 6.93 (meta, para)
6	7.04	3.67	2.07, 1.92	PEt$_3$: 1.82 (methylene); 1.19 (methyl)
7	6.82	3.41	2.03, 1.62	dppp: 7.71 (ortho); 7.02 (meta, para); 2.64 (CH$_2$P); 2.17 (C*H*$_2$(CH$_2$P)$_2$)
8	7.04	3.72	2.03	COD: 3.91 (vinyl); 2.21, 1.64 (methylene)
9	6.67	3.17	1.66	
10	6.76	3.34	1.87, 1.41	PPh$_3$: 7.87 (ortho); 7.01 (meta, para)
11	6.79	3.44	1.32	PPh$_3$: 7.88 (ortho); 6.93 (meta, para)
12	7.0	3.41	1.94, 1.65	allyl: 6.17 (central vinyl); 4.94 (terminal vinyl); 2.91, 2.58 (methylene) PPh$_3$: 7.90 (ortho); 6.9–7.1 (meta, para)
13	6.9–7.4	3.39	1.64, 1.63	CH$_2$Ph: 6.9–7.4 (aromatics); 3.48, 2.96 (methylene) PPh$_3$: 7.94 (ortho), 6.9–7.4 (meta, para)

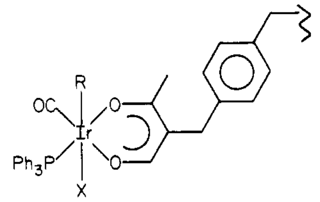


complex	H^a	H^b	others
14	5.12	1.70	COD: 4.31 (vinyl); 2.21, 1.54 (methylene)
15	5.06	1.52	
16	5.31	1.29	PPh$_3$: 7.84 (ortho); 6.92 (meta, para)
17	5.20	1.80, 1.50	allyl: 6.1 (central vinyl); 4.9 (terminal vinyls); 2.85, 2.45 (methylene)

iridium-bound –CH$_2$– group. The α-methylene hydrogens are geminally coupled (J_{gem} = 9.3 Hz) and both are coupled to the vicinal vinyl hydrogen (J_{vic} = 6.4 Hz). The methylene resonance which appears at 2.91 ppm contains, in addition to the above couplings, a phosphorus coupling of 4.4 Hz. The observation of phosphorus coupling to only one of the methylene hydrogens suggests that the allyl group is held in a specific orientation with rotation about the metal–carbon bond restricted, possibly as a result of the presence of the bulky phosphine ligand. A similar coupling pattern is observed for the iridium(III) benzyl complex, **13**.

The reaction of **10** with benzyl bromide results in the oxidative addition of the alkyl halide and the formation of the iridium(III) benzyl complex, **13**. As observed for complex **12**, the IR spectrum of **13** indicates the formation of an iridium(III) carbonyl complex by the appearance of ν_{CO} at 2034 cm^{-1}. In the ^{1}H NMR spectrum of **13**, two multiplets are observed which are assigned to nonequivalent benzylic hydrogens. Both resonances contain geminal coupling of 9.5 Hz, in addition to phosphorus coupling. The upfield resonance has a coupling to phosphorus of 2.4 Hz, and the downfield resonance has J_{P-H} = 3.5 Hz.

The iridium(III) centers in complexes **12** and **13** are assigned octahedral coordination geometries. On the basis of the known trans stereochemistry of RX oxidative addition, as shown, for example, by the trans addition of MeI to Rh(PPh$_3$)$_2$(acac),[14] we assign the structures of **12** and **13** as II, where R = σ-allyl, benzyl.

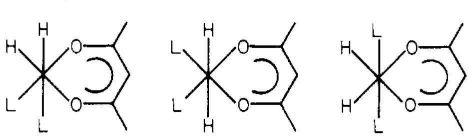


II

The oxidative addition of allyl bromide to the mononuclear analogue, Ir(CO)(PPh$_3$)(acac), was also examined. This reaction produces the iridium(III) allyl complex **17**. Its IR spectrum shows a band at 2040 cm^{-1} due to ν_{CO} and bands at 1568 and 1520 cm^{-1} assignable to the chelating acac group. The ^{1}H NMR spectrum of **17** contains resonances due to coordinated triphenylphosphine at 7.9 and 6.96 ppm. The acac ligand has resonances at 5.21, 1.81, and 1.52 ppm due, respectively, to the central methine proton and the two inequivalent methyl groups. The σ-allyl group has resonances fairly similar to those of the binuclear species, **12**. A multiplet appears at 6.1 ppm, assignable to the central vinylic proton, while the terminal vinyl protons appear at 4.9 ppm as overlapping multiplets. The downfield methylene resonance at 2.85 contains geminal coupling of 8.2 Hz, phosphine coupling of 4.2 Hz, and vicinal coupling to the vinyl proton of 6.5 Hz. The upfield α-methylene resonance contains geminal coupling and coupling to the vinyl proton of 6.4 Hz.

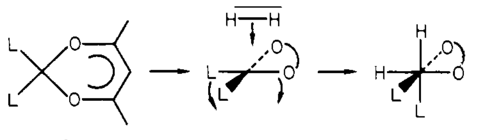
Reactions with H$_2$. In order to determine the potential activity of the binuclear iridium complexes **8**–**11** as homogeneous hydrogenation catalysts, we set out to examine their reactivity with H$_2$. Studies by Arâneo have shown that the complex IrH$_2$(PPh$_3$)$_2$(acac) (**18**) forms via the reaction of IrH$_3$(PPh$_3$)$_2$ with Hacac.[18] As a starting point for our studies, we prepared the iridium complex, Ir(PPh$_3$)$_2$(acac) (**16**), and examined its reaction with H$_2$. The complex IrH$_2$(PPh$_3$)$_2$(acac) (**18**) is formed from the reaction of **16** + H$_2$ and is identified by its ^{1}H NMR spectrum and comparison with the previously reported spectrum[18] (δ_{Ir-H} = –24.7, t, J = 17.1 Hz).

Three stereochemistries are possible for complex **18**, shown as III–V, and on the basis of the observed chemical shift and coupling constants for the iridium hydride, complex **18** is assigned structure V.



III IV V

However, the initially formed H$_2$ addition product cannot have the stereochemistry shown as V if the addition is a cis-concerted addition and occurs on a face of the square plane with mutually trans ligands bending out of the square plane away from the addend H$_2$ as shown in eq 2. This reaction



(2)

results in the formation of the isomer whose stereochemistry is shown as III. If the oxidative addition were to occur in this

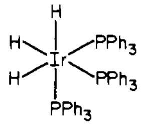
---

(18) Arâneo, A. *Gazz. Chim. Ital.* **1965**, *95*, 1431.

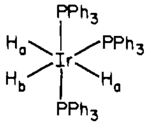
Inorg. Chem. **1984**, *23*, 1703–1708

fashion, then the dihydride species III which initially forms rearranges to give the observed product, V. An alternative explanation to account for the observed product is the oxidative addition of H_2 to an iridium species other than $Ir(PPh_3)_2(acac)$, possibly via loss of phosphine prior to oxidative addition.

During the course of the reaction of **16** + H_2, several other hydride resonances are observed in the −8 to −14 ppm region of the ^1H NMR spectrum. If the iridium(I) bis(phosphine) complex, **16**, is prepared in situ from Ir(COD)(acac) + PPh_3 under H_2, these hydride resonances are much more evident. On the basis of the observed coupling constants as determined through selective homonuclear decoupling, we identify these additional hydride resonances as belonging to the *fac* and *mer* isomers of the iridium(III) trihydride complex, $IrH_3(PPh_3)_3$, shown as structures VI and VII, respectively.



VI



VII

In the ^1H NMR spectrum of the facial isomer, VI, the equivalent hydrides appear as a complex multiplet centered at −11.38 ppm, which contain a large trans-phosphorus coupling of 120 Hz and a smaller cis-phosphorus coupling of ca. 18 Hz. The spectrum of the meridional isomer, VII, exhibits two complex multiplets at −10.2 and −12.1 ppm. The H_b multiplet (−12.1 ppm) contains a large trans-phosphorus coupling of 116 Hz and J_{cis-P} of 22 Hz, while proton H_a gives rise to an apparent quartet with a cis-phosphorus coupling of 16 Hz.[19] Comparison of the hydride spectra of VI and VII with the spectra of the closely related iridium complexes $IrH_3(PEt_2Ph)_3$ and $IrH_3(PEt_3)_3$[20] confirms our structural assignments.

The formation of these iridium(III) trihydride complexes, VI and VII, requires the loss of the acac ligand from the metal center. The presence of free triphenylphosphine facilitates this displacement and increases the amount of $IrH_3(PPh_3)_3$ formed during the reaction H_2 + Ir(COD)(acac) + PPh_3. These same iridium hydride complexes, VI and VII, are observed during the reaction of the binuclear iridium complex **8** with H_2 and PPh_3. It is thus apparent that both the binucleating bis(β-diketonate) ligand, $xyl(acac)_2$, and the simple bidentate ligand, acac, are easily displaced by H_2 as well as by H^+. These observations, together with our results on the activity and stability of the rhodium complexes $Rh(P(OPh)_3)_2(acac)$[16] and $(Rh(P(OPh)_3)_2)_2(xyl(acac)_2)$, indicate that a binuclear framework using $xyl(acac)_2$ complexes of Rh and Ir will not be maintained during simple catalytic reactions such as olefin hydrogenation and hydroformylation.

Acknowledgment. We wish to thank the National Science Foundation (Grants CHE 80-11974 and CHE 83-08064) and the Office of Naval Research for support of this work. A generous loan of precious metal salts from Johnson Matthey Co., Inc., is also gratefully acknowledged. B.C.W. acknowledges a Sherman Clarke Fellowship.

Registry No. **1**, 89890-61-9; **2**, 89890-62-0; **3**, 89890-63-1; **4**, 89890-64-2; **5**, 89890-65-3; **6**, 89890-66-4; **7** (monomer), 89890-67-5; **7** (dimer), 89890-76-6; **8**, 89890-68-6; **9**, 89890-69-7; **10**, 89890-70-0; **11**, 89890-71-1; **12**, 89890-72-2; **13**, 89890-73-3; **14**, 12154-84-6; **15**, 14023-80-4; **16**, 89890-74-4; **17**, 89890-75-5; **18**, 64625-61-2; $[Ir(\mu\text{-}Cl)(1,5\text{-}COD)]_2$, 12112-67-3; $Rh_2(COD)_2(\mu\text{-}Cl)_2$, 12092-47-6; *fac*-$IrH_3(PPh_3)_3$, 18660-46-3; *mer*-$IrH_3(PPh_3)_3$, 18660-47-4; C_3H_6, 115-07-1.

---

(19) Irradiation of the resonance due to H_a results in the complete disappearance of the resonance due to H_b. This suggests that the hydride ligands in *mer*-$IrH_3(PPh_3)_2$ interconvert at room temperature. On the basis of the frequency separation between the two resonances of 720 Hz, the rate of exchange must be slower than 1.4×10^{-3} s, but this interconversion must be faster than the rate of relaxation (T_1) of the hydride ligands in order to cause the saturation of both H_a and H_b during the decoupling experiment.

(20) Mann, B. E.; Masters, C.; Shaw, B. L. *J. Inorg. Nucl. Chem.* **1971**, *33*, 2195.

Contribution from the Department of Inorganic Chemistry,
University of Melbourne, Parkville, Victoria, 3052 Australia

Altruism Revisited: Gas Electron Diffraction Study of Tris(trifluoromethyl)phosphine Oxide, $OP(CF_3)_3$, and ab Initio Molecular Orbital Calculations on X_3C–Y and X_3C–Y(O) Systems (X = H, F; Y = PH_2, SH, Cl)

COLIN J. MARSDEN

Received May 18, 1983

The molecular structure of tris(trifluoromethyl)phosphine oxide, $OP(CF_3)_3$, has been investigated by gas-phase electron diffraction. Principal structural parameters, with uncertainties (2σ) in parentheses, are r_g(C–F) = 1.336 (2) Å, r_g(P–C) = 1.897 (4) Å, r_g(P═O) = 1.476 (8) Å, ∠O–P–C = 114.2 (0.4)°, ∠C–P–C = 104.3 (0.4)°, ∠P–C–F = 110.4 (0.2)°, and ∠F–C–F = 108.5 (0.2)°. CF_3 groups appear to be tilted by 1.9 (1.2)° away from the P═O bond and twisted by 16.2 (2.0)° away from a staggered conformation. Shrinkage corrections and amplitudes of vibration, which agreed satisfactorily with measured amplitudes, were calculated from an approximate force field. The vibrational spectrum was extended to low frequencies to include some bending modes previously unreported. Phosphorus–carbon bonds are substantially longer than in $OP(CH_3)_3$, and the lengthening is greater than that found for $P(CF_3)_3$. The concept of "altruistic bonding", involving the 3d orbitals on phosphorus, previously advanced to account for the long P–C bonds in $P(CF_3)_3$, is examined in the light of extensive ab initio MO calculations on CH_3 and CF_3 derivatives of phosphorus, sulfur, and chlorine.

Introduction

In a recent reinvestigation of the structure of $P(CF_3)_3$,[1] the P–C bond length was confirmed to be appreciably greater than that in $P(CH_3)_3$. This observation provided another example of the curious striking trends in $(F_3)C$–X bond distances,[2,3] which are shorter than $(H_3)C$–X if X is highly electronegative but longer if X is of moderate to low electronegativity.

---

(1) C. J. Marsden and L. S. Bartell, *Inorg. Chem.*, **15**, 2715 (1976).

(2) C. J. Marsden and G. M. Sheldrick, *J. Mol. Struct.*, **10**, 419 (1971).

(3) A. Yokozeki and S. H. Bauer, *Top. Curr. Chem.*, **53**, 71 (1975).

0020-1669/84/1323-1703$01.50/0