spectrum showed 10% of the free ligand in addition to the complex. No other products were noted.

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

Supplementary Material Available: Table V, listing equations of planes, Table VII, listing hydrogen positional parameters for 14, and Table VIII, listing anisotropic thermal parameters for 14 (3 pages); a table of calculated and observed structure factors for 14 (6 pages). Ordering information is given on any current masthead page.

Chemistry of Iridium(I) and Rhodium(I) Compounds Containing Pyridylmethyl Ligation

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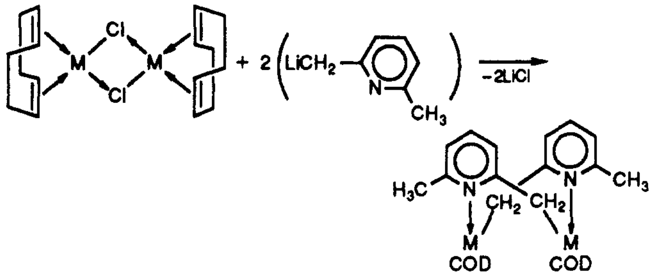
Received January 8, 1990

Treatment of the chloro-bridged dimers $[(COD)M(\mu\text{-}Cl)]_2$ (M = Rh, Ir; COD = 1,5-cyclooctadiene) with [(6-methyl-2-pyridyl)methyl]lithium ($Li\text{-}CH_2\text{-}py\text{-}6Me$) leads to the formation of the dinuclear compounds $[(COD)M(\mu\text{-}CH_2\text{-}py\text{-}6Me\text{-}C,N)]_2$ (M = Rh, **1**; Ir, **2**) in high yields. The solid-state structures of orange **1** and red **2** show the compounds to possess an "open book" type structure consisting of two square planes held together by the pyridylmethyl bridges similar to the known hydroxypyridinato analogues. A long metal–metal distance of 3.6806 (3) Å for **1** and 3.5889 (3) Å for **2** indicates little interaction between adjacent square planes. Treatment of iridium compound **2** with $EtPPh_2$ did not lead to displacement of the COD ligand. Instead formation of the mononuclear compound $(COD)Ir(EtPPh_2)_2(CH_2\text{-}py\text{-}6Me)$ (**3**) takes place. A solid-state structural analysis of **3** confirmed the stoichiometry and showed the pyridylmethyl group to be only carbon bound with a five-coordinate (18-electron) iridium metal center. Attempts to form new binuclear species by reaction of **1** and **2** with dppm ($Ph_2PCH_2PPh_2$) led instead to new compounds of formula [(dppm)M(dppm-H)] (M = Rh, **4**; Ir, **5**). In this reaction, the pyridylmethyl group has acted as an intramolecular base, leading to deprotonation of the methylene group of one of the dppm ligands and formation of 2,6-dimethylpyridine. A single-crystal X-ray diffraction study of rhodium complex **4** showed a square-planar rhodium(I) center chelated through the phosphorus atoms of both dppm and its deprotonated, methanide form. Crystal data for $Rh_2N_2C_{30}H_{40}$ (**1**) at 20 °C are $a = 7.529$ (1) Å, $b = 10.667$ (1) Å, $c = 16.573$ (2) Å, $\alpha = 83.620$ (9)°, $\beta = 80.93$ (1)°, $\gamma = 84.86$ (1)°, $Z = 2$, $d_{calcd} = 1.617$ g cm^{-3} in space group $P\bar{1}$; for $Ir_2N_2C_{30}H_{40}$ (**2**) at 20 °C are $a = 7.5369$ (8) Å, $b = 10.6727$ (6) Å $c = 16.482$ (2) Å, $\alpha = 85.020$ (6)°, $Z = 2$, $d_{calcd} = 2.082$ g cm^{-3} in space group $P\bar{1}$; for $IrP_2NC_{43}H_{50}$ (**3**) at 20 °C are $a = 11.236$ (2) Å, $b = 13.663$ (50) Å, $c = 13.809$ (3) Å, $\alpha = 64.40$ (2)°, $\beta = 78.33$ (2)°, $\gamma = 80.68$ (2)°, $Z = 2$, $d_{calcd} = 1.486$ g cm^{-3} in space group $P\bar{1}$; and for $RhP_4C_{62}H_{55}\cdot 2C_6H_6$ (4) at −43 °C are $a = 29.793$ (5) Å, $b = 10.055$ (3) Å, $c = 18.666$ (3) Å, $\beta = 114.00$ (2)°, $Z = 4$, $d_{calcd} = 1.335$ g cm^{-3} in space group *Cc*.

Introduction

One of the most interesting developments in transition-metal chemistry over the last 15 years has been in the area of dinuclear systems.[1] Pivotal to this exploration has been the use of binuleating ligation, which has the correct geometry to hold the two metal centers close to each other.[2,3] In an attempt at the rational synthesis of mixed-metal binuclear compounds containing early and late d-block metals, we have isolated a series of group 4 metal compounds containing pyridylmethyl ligation; e.g., $(ArO)_2M(CH_2\text{-}py\text{-}6Me)_2$ and $Cp_2M(CH_2\text{-}py\text{-}6Me)_2$ (M = Zr, Hf; CH_2-py-6Me = (6-methyl-2-pyridyl)methyl).[4,5]

Scheme I



1, 2

Attempts to incorporate either rhodium(I) or iridium(I) into these systems by coordination through the pyridyl

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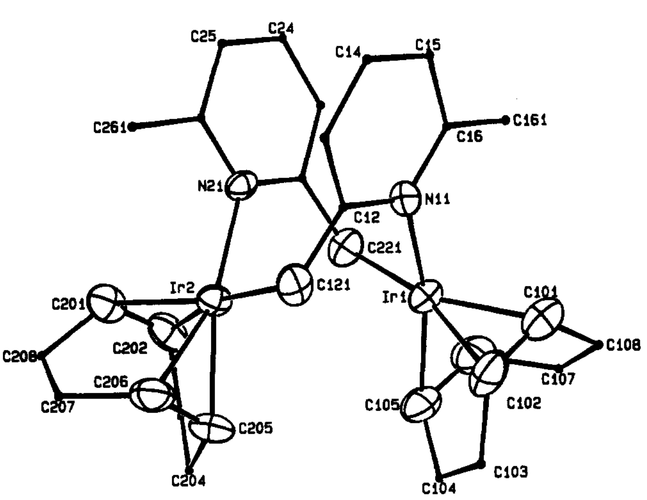


Figure 1. ORTEP view of $[(COD)Rh(\mu\text{-}CH_2\text{-}py\text{-}6Me\text{-}C,N)]_2$ (1). The labeling scheme for isomorphous 2 is identical.

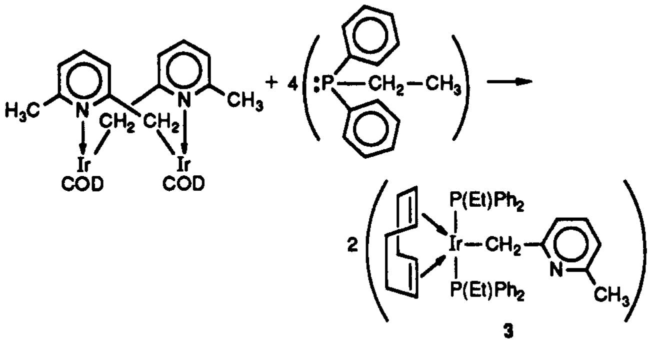
Table I. Selected Bond Distances (Å) and Angles (deg) for $[(COD)M(\eta^2\text{-}CH_2\text{-}py\text{-}6Me\text{-}C,N)]_2$ (M = Rh, 1; Ir, 2)

	1	2
M(1)-M(2)	3.6806 (3)	3.5889 (3)
M(1)-N(11)	2.118 (2)	2.103 (6)
M(1)-C(221)	2.137 (3)	2.128 (7)
M(2)-N(21)	2.118 (2)	2.104 (5)
M(2)-C(121)	2.130 (3)	2.128 (7)
M(1)-C(101)	2.148 (4)	2.129 (9)
M(1)-C(102)	2.173 (4)	2.167 (8)
M(1)-C(105)	2.107 (3)	2.110 (8)
M(1)-C(106)	2.119 (3)	2.113 (9)
M(2)-C(201)	2.168 (3)	2.147 (7)
M(2)-C(202)	2.163 (3)	2.146 (7)
M(2)-C(205)	2.115 (3)	2.099 (7)
M(2)-C(206)	2.108 (3)	2.101 (7)
N(11)-M(1)-C(221)	90.2 (1)	90.9 (2)
N(11)-M(2)-C(121)	90.0 (1)	90.6 (2)
M(1)-C(221)-C(22)	116.6 (2)	116.5 (5)
M(2)-C(121)-C(12)	117.2 (2)	117.7 (5)

nitrogen have so far failed. instead complete transfer of the pyridylmethyl ligation has been observed, leading to a new series of binuclear, pyridylmethyl-bridged derivatives of Rh(I) and Ir(I). We wish to report here upon the structures and reactivity of these new binuclear systems.

Results and Discussion

Scheme II



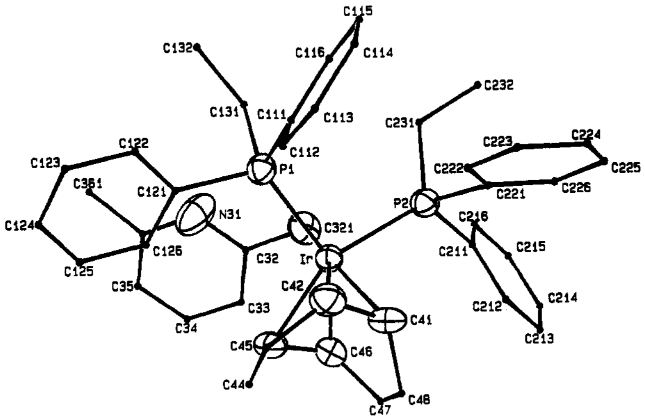


Figure 2. ORTEP view of $[(COD)Ir(PEtPh_2)_2(CH_2\text{-}py\text{-}6Me)]$ (3).

Table II. Selected Bond Distances (Å) and Angles (deg) for $[(COD)Ir(CH_2\text{-}py\text{-}6Me)(PEtPh_2)_2]$ (3)

Ir-P(1)	2.406 (2)	Ir-P(2)	2.332 (2)
Ir-C(320)	2.200 (6)	Ir-C(41)	2.228 (6)
Ir-C(42)	2.244 (6)	Ir-C(45)	2.149 (6)
Ir-C(46)	2.131 (6)	C(42)-C(42)	1.383 (2)
C(45)-C(46)	1.414 (9)		
P(1)-Ir-P(2)	100.88 (5)	P(1)-Ir-C(321)	90.0 (2)
P(2)-Ir-C(321)	84.5 (2)	C(321)-Ir-C(41)	154.2 (2)
C(321)-Ir-C(42)	165.1 (2)	C(321)-Ir-C(45)	89.8 (2)
C(321)-Ir-C(46)	83.5 (2)		

Reaction of the chloro-bridged dimers $[(COD)MCl]_2$(M = Rh, Ir; COD = 1,5-cyclooctadiene) with either $Cp_2Hf(CH_2\text{-}py\text{-}6Me)_2$ or $Cp_2Hf(CH_2\text{-}py\text{-}6Me)Cl$[4] in hydrocarbon solvents leads to the formation of the compounds $[(COD)M(\mu\text{-}CH_2\text{-}py\text{-}6Me\text{-}C,N)]_2$(M = Rh, 1; Ir, 2) along with Cp_2HfCl_2. Carrying out the reaction in d_6-benzene solvent allowed the formation of the products to be monitored by ^1H NMR spectroscopy. No intermediates could be detected, the formation of either 1 or 2 along with Cp_2HfCl_2 taking place rapidly. The formation of 1 and 2 is also achieved in higher yields by treatment of the corresponding chloro-bridged dimers with $Li\text{-}CH_2\text{-}py\text{-}6Me$ in hydrocarbon solvents (Scheme I). Compounds 1 and 2 can be readily recrystallized from toluene as large orange 1 and red 2 blocks. A single-crystal X-ray analysis of 1 and 2 showed the compounds to be isomorphous and contain the two pyridylmethyl groups bridging the two metal centers in a head-to-tail fashion (Figure 1).[6-8] Some selected bond distances and angles for the rhodium and iridium compounds are compared in Table I. The structures of 1 and 2 are closely related to the 6-methyl-2-hydroxypyridinate (mhp) complexes $[(COD)M(\mu\text{-}mhp)]_2$ reported by Mann et al.[6] as well as the extensively studied pyrazolyl-bridged species.[9] However, in the alkyl compounds 1 and 2, the two metal-centered square planes are held further apart, c.f. M–M distances of 3.6806 (3) and 3.5889 (3) Å for 1 and 2 versus 3.242 (1) and 3.367 (1) Å for the corresponding pyridinato derivatives.[6] The ^1H and ^{13}C NMR spectra of 1 and 2 clearly indicate the nonequivalence of all eight carbon atoms of the COD ligands

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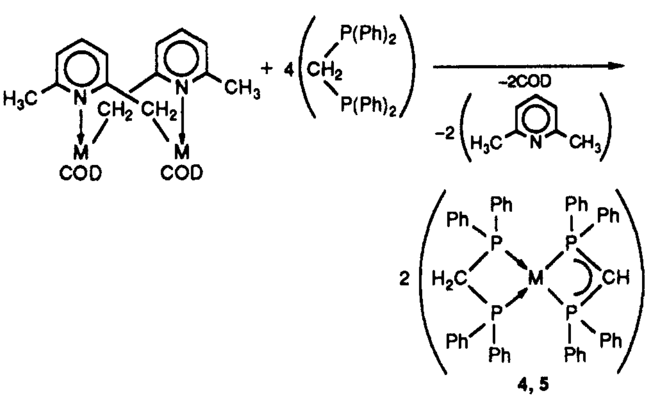
Scheme III



in solution.[11] Furthermore, the presence of the methylene group, CH_2-py-6Me, as a sharp AB pattern in the ^1H NMR spectrum implies that the dinuclear solid-state structure is maintained in solution.[6] Hence, the pyridylmethyl-bridged dinuclear units in 1 and 2 do not undergo facile fragmentation into 16-electron mononuclear units such as [(COD)M(CH_2-py-6Me-*C,N*)]. The square-planar geometry about each metal center in compounds 1 and 2 results in one COD olefinic bond being trans to an alkyl carbon while the other olefinic bond is trans to a pyridine nitrogen. A pronounced trans infuence can be seen from the structural data (Table I). The M–C (COD) distances are 0.04–0.05 Å longer for the atoms trans to the alkyl carbon. Also consistent with this picture is the fact that the olefinic carbon–carbon distances are slightly (0.02 Å) longer for the olefinic bond trans to the pyridine nitrogen.

The reaction of the dinulcear compounds 1 and 2 with various phosphine ligands has been investigated. In most cases, a mixture of products was indicated by ^1H NMR spectra of the reaction products. However, treatment of iridium complex 2 with $PEtPh_2$ was found to lead to formation of the mononuclear derivative [(COD)Ir($PEtPh_2$)$_2$(CH_2-py-6Me)] (3) (Scheme II).[10] The molecular structure of 3 (Figure 2, Table II)[13] is best described as a distorted trigonal bipyramid with the carbon atom of the purely C-bond pyridylmethyl group and one of the COD olefinic bonds occupying axial sites. The two phosphorus atoms of the $PEtPh_2$ ligands and the remaining COD olefinic group then can be considered as occupying the equatorial sites. The Ir–C bond lengths to the olefinic carbon atoms trans to the pyridylmethyl group, 2.228 (6) and 2.244 (6) Å, are definitely longer than to the equatorial ones, 2.131 (6) and 2.149 (6) Å (Table II). The Ir–CH_2–py angle of 117.7 (4)° places the pyridine nitrogen atom well away from the metal center and contrasts with values of <90° when the group is chelated to the same metal center.[4,5] In solution at ambient temperatures, the ^1H NMR spectra of 3 are very broad except for the pyridylmethyl resonances which are sharp. The CH_2-py-6Me methylene group appears as a singlet at room temperature with no evidence of coupling to the ^{31}P nuclei of the phosphine ligands. However, on cooling solutions of 3, the COD and $PEtPh_2$ resonances sharpen up and begin to resolve while the methylene group splits into a broad triplet with $^3J(^{31}P-^1H) = 10$ Hz. We interpret these results in terms of rapid dissociation and recoordination of the phosphine ligands taking place at room temperature, leading to loss of coupling between the methylene protons and phosphorus.

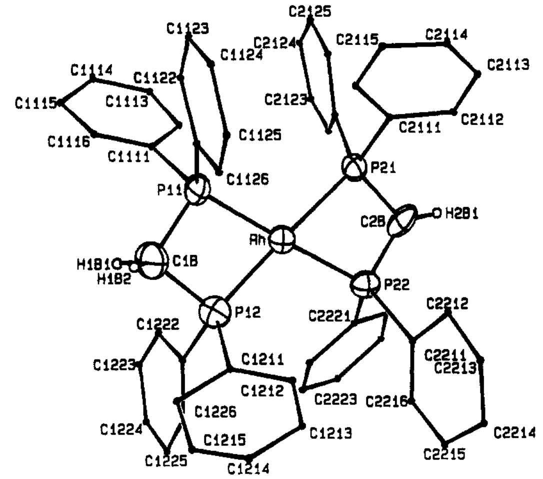


Figure 3. ORTEP view of [(dppm)Rh(dppm-H)] (4).

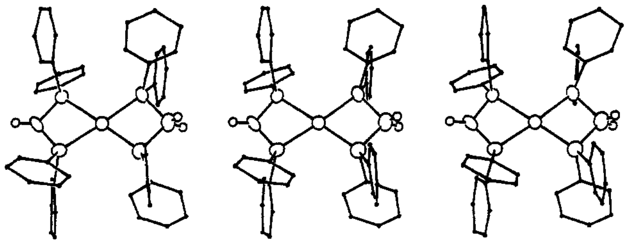


Figure 4. ORTEP view showing the orientation of the square-planar units in the solid-state structure of 4.

Table III. Selected Bond Distances (Å) and Angles (deg) for [(dppm)Rh(dppm-H)] (4)

Rh–P(11)	2.293 (3)	Rh–P(12)	2.237 (4)
Rh–P(21)	2.342 (3)	Rh–P(22)	2.324 (3)
P(11)–C(1b)	1.85 (1)	P(12)–C(1b)	1.84 (1)
P(21)–C(2b)	1.76 (1)	P(22)–C(2b)	1.68 (1)
P(11)–Rh–P(12)	72.84 (4)	P(21)–Rh–P(22)	69.23 (3)
Rh–P(11)–C(1b)	95.7 (4)	Rh–P(12)–C(1b)	97.8 (5)
Rh–P(11)–C(2b)	93.6 (4)	Rh–P(22)–C(2b)	96.4 (3)
P(11)–C(1b)–P(12)	93.6 (2)	P(21)–C(2b)–P(22)	100.7 (2)

Reaction of benzene solutions of the binuclear complexes 1 and 2 with the potentially binucleating ligand dppm ($Ph_2PCH_2PPh_2$) initially leads to a reaction mixture whose components we have been unable to identify. However, over a period of hours, deep-red, well-formed crystals of a sparingly soluble new compounds (M = Rh, 4; Ir, 5) precipitate from the solution (Scheme III). In order to maximize the yield of 4 and 5, it was found necessary to add 2 equiv of dppm per metal center. Both compounds 4 and 5 gave mass spectra that showed a strong molecular ion corresponding to $[(dppm)M(dppm-H)]^+$. The crystals obtained from the benzene reaction solvent were found to possess significant amounts of benzene solvate molecules which were lost either upon drying or washing with hexane. However, a crystal of 4 suitable for crystallographic analysis was finally obtained direct from the mother liquor and a single-crystal X-ray diffraction analysis carried out (Figure 3, Table III). The molecule can be seen to consist of discrete square-planar rhodium units in which the metal atom is chelated by both dppm as well as its deprotonated,

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Table IV. Crystal Data and Data Collection Parameters

	1	2	3	4
formula	$Rh_2N_2C_{30}H_{40}$	$Ir_2N_2C_{30}H_{40}$	$IrP_2NC_{43}H_{50}$	$RhP_4C_{62}H_{55}$
fw	634.48	813.07	835.03	1026.93
space group	$P\bar{1}$ (no. 2)	$P\bar{1}$	$P\bar{1}$	*Cc* (no. 9)
a, Å	7.529 (1)	7.5369 (8)	11.236 (2)	29.793 (5)
b, Å	10.667 (1)	10.6727 (6)	13.663 (5)	10.055 (3)
c, Å	16.573 (2)	16.482 (2)	13.809 (3)	18.666 (3)
α, deg	83.620 (9)	83.569 (7)	64.40 (2)	90
β, deg	80.93 (1)	80.66 (1)	78.33 (2)	114.00 (2)
γ, deg	84.86 (1)	85.020 (6)	80.68 (2)	90
V, $Å^3$	1302.8 (4)	1296.8 (3)	1865.7 (9)	5108 (4)
Z	2	2	2	4
d_{calcd}, g cm^{-3}	1.617	2.082	1.486	1.335
crystal dimens, mm	0.44 × 0.39 × 0.38	0.25 × 0.25 × 0.22	0.47 × 0.45 × 0.28	0.52 × 0.45 × 0.24
temp, °C	20	20	20	−43
radiation (wavelength)	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)
monochromator	graphite	graphite	graphite	graphite
linear abs coeff, cm^{-1}	12.68	102.35	36.78	4.90
abs corrn applied	empirical[a]	empirical[a]	empirical[a]	empirical[a]
transmissn factors: min, max	0.79, 1.00	0.84, 1.00	0.67, 1.00	0.68, 1.00
diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Enraf-Nonius CAD4
scan method	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
hkl limits	−7 to 8, −11, to 11, 0 to 17	−7 to 8, −11 to 11, 0 to 17	−11 to 12, −12 to 14, 0 to 14	0 to 32, 0 to 10, −20 to 18
2θ range, deg	4.00–45.00	4.00–45.00	4.00–45.00	4.00–45.00
scan width, deg	$0.43 + 0.35 \tan \theta$	$0.43 + 0.35 \tan \theta$	$1.16 + 0.35 \tan \theta$	$0.49 + 0.35 \tan \theta$
take-off angle, deg	3.15	1.90	3.15	3.15
programs used	Enraf-Nonius SDP	Enraf-Nonius SDP	Enraf-Nonius SDP	Enraf-Nonius SDP
F_{000}	648.0	776.0	844.0	2128.0
p factor used in weighting	0.040	0.040	0.040	0.040
data collected	3390	3367	4857	3557
unique data	3390	3367	4857	3557
data with $I > 3.0\sigma(I)$	3082	2795	4032	2982
no. of variables	307	307	424	602
largest shift/esd in final cycle	0.00	0.01	0.01	0.89
R	0.026	0.021	0.028	0.029
R_w	0.039	0.027	0.037	0.038
GOF	1.501	0.915	1.219	1.430

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methanide conjugate base. In the lattice, the square-planar units are arranged coplanar with the CH_2 group of one dppm ligand next to the CH group of a dppm-H ligand on the adjacent unit (Figure 4). These chains are then separated by benzene molecules above and below the square plane ($2C_6H_6$ per Rh) so that no metal–metal interaction takes place through the faces of the square planes. Compounds 4 and 5 represent new memers of a growing class of compounds containing deprotonated dppm ligands.[11-20] However, an interesting feature of these molecules is that they contain both dppm and dppm-H chelated to the same metal. The two groups are differentiated by significantly shorter Rh–P and P–C distances for the methanide ligand (Table III). In the ^1H and NMR spectra of sparingly soluble 4 and 5, the C*H* proton of the dppm-H ligand can be readily observed resonating upfield of the CH_2 protons of the normal dppm ligand. In the ^{31}P NMR spectrum of 4, a complex AA′BB′X pattern is observed due to coupling between the two types of phosphorus atoms as well as the ^{103}Rh metal center.

The formation of **4** and **5** from **1** and **2**, respectively, involves the deprotonation of a dppm methylene group by pyridylmethyl ligation. The formation of 2,6-dimethylpyridine was identified in the reaction mixture by ^1H NMR spectroscopy. Attempts to convert the chloro-bridged dimers $[(COD)M(\mu\text{-}Cl)]_2$ (M = Rh, Ir) into **4** and **5** by treatment with dppm in the presence of a base, e.g., $LiCH_3$, LiOPh, and $LiNMe_2$, have so far failed.

Experimental Section

All reactions and manipulations were carried out under dry nitrogen atmosphere or in vacuo either in a Vacuum Atmosphere Dri-Lab or by standard Schlenk techniques. Hydrocarbon solvents and ether were dried by distillation from sodium benzophenone and stored under nitrogen. $Li\text{-}CH_2\text{-}py\text{-}6Me$ was prepared by reaction of 2,6-lutidine and 1 equiv of $LiBu^n$. 1,5-Cyclooctadiene was purchased from Aldrich and used without further purification. Dimethylphenylphosphine, and bis(diphenylphosphino)methane were purchased from Strem Chemicals. $[(COD)M(\mu\text{-}Cl)]_2$ was made by published procedures (M = Ir, Rh).[21] ^1H and ^{13}C NMR spectra were recorded on Varian Assoc. Gemini 200, General Electric QE 300, Varian Assoc. Gemini 200, and Perkin-Elmer R32 spectrometers. Infrared spectra were recorded by using a Perkin-Elmer FT 1800 spectrophotometer.

$[(COD)Rh(\mu\text{-}CH_2\text{-}py\text{-}6Me\text{-}C,N)]_2$ (1). To a solution of $[(COD)Rh(\mu\text{-}Cl)]_2$ (0.300 g, 0.61 mmol) in benzene (15 mL) was slowly added solid $Li\text{-}CH_2\text{-}py\text{-}6Me$ (0.147 g, 1.3 mmol) with stirring. After 8 h the reaction mixture was filtered and the filtrate evaporated to dryness under vacuum. The crude product was

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obtained as large yellow crystals by cooling a saturated toluene solution. Yield = 0.316 g (82%). Anal. Calcd for $Rh_2N_2C_{30}H_{40}$: C, 56.79; H, 6.35; N, 4.41. Found: C, 56.95; H, 6.53; N, 4.67. ^{1}H NMR (C_6D_6, 30 °C): δ 2.39 (dd), 4.22 (dd, Rh-C*H*$_2$-py-6Me); 2.68 (s, 6 *Me*); 3.87 (m), 3.89 (m), 4.06 (m), 4.22 (m, COD-C*H*); 1.8–3.0 (overlapping multiplets, COD-C*H*$_2$); 5.85 (d), 6.36 (d), 6.56 (t, 3,5,4-*H* of py). ^{13}C NMR (C_6D_6, 30 °C): δ 10.5 (d, Rh-*C*h$_2$-py-6Me, $^{1}J(^{103}Rh–^{13}C)$ = 21 Hz); 19.2 (6*Me*); 30.2, 30.9, 32.3, 32.8 (COD-*C*H$_2$); 74.6 (d, $^{1}J(^{103}Rh–^{13}C)$ = 14 Hz), 75.5 (d, $^{1}J(^{103}Rh–^{13}C)$ = 15 Hz), 83.1 (d, $^{1}J(^{103}Rh–^{13}C)$ = 8.6 Hz), 84.1 (d, $^{1}J(^{103}Rh–^{13}C)$ = 9 Hz) (COD-*C*H).

[(COD)Ir(μ-CH$_2$-py-6Me-*C*,*N*)]$_2$ (2). An essentially identical procedure was followed as for **1** only with [(COD)Ir(μ-Cl)]$_2$ (0.20 g, 0.30 mmol) and Li-CH$_2$-py-6Me (0.08 g, 0.65 mmol). Yield of the red crystalline blocks of **2** from toluene = 0.21 g (85%). Anal. Calcd for $Ir_2N_2C_{30}H_{40}$: C, 44.31; H, 4.95; N, 3.44. Found: C, 44.68; H, 5.14; N, 3.36. ^{1}H NMR (C_6D_6, 30 °C): δ 3.11 (d), 4.29 (d, Ir-C*H*$_2$-py-6Me); 2.51 (s, 6 *Me*); 3.10 (m), 3.21 (m), 3.70 (m), 4.11 (m, COD-C*H*); 1.5–3.0 (overlapping multiplets, COD-C*H*$_2$); 5.79 (d), 6.23 (d), 6.48 (t, 3,5,4-H of py). ^{13}C NMR (C_6D_6, 30 °C): δ 30.7 (Ir-*C*H$_2$-py-6Me); 24.0 (*Me*); 29.1, 30.0 30.7, 31.5 (COD-*C*H$_2$); 57.4, 60.1, 63.2, 66.1 (COD-*C*H).

[(COD)Ir(CH$_2$-py-6Me)(PEtPH$_2$)$_2$] (3). To a solution of **2** (0.12 g, 0.15 mmol) in benzene (10 mL) was added PEtPh$_2$ (0.14 g, 0.65 mmol) in benzene (5 mL). The initially dark red mixture lightened to pale yellow over minutes. Removal of solvent under vacuum yielded a yellow oil, which was taken up in hot hexane. Upon slow cooling of the hexane solution, crystals of **3** were obtained. Yield = 0.22 g (87%). Anal. Calcd for $IrP_2NC_{43}H_{50}$: C, 61.85; H, 6.03; N, 1.67; P, 7.41. Found: C, 61.71; H, 5.95; N, 1.67; P, 7.80. ^{1}H NMR (C_6D_6, −20 °C): δ 3.10 (t, Ir–CH$_2$, $^{3}J(^{31}P–^{1}H)$ = 10 Hz); 2.20 (s, 6 *Me*); 6.4 (d), 6.5 (d), 6.8 (t, 3,5,4-*H* of py); 1.4–1.9 (overlapping m, COD-C*H*$_2$); 3.0–3.6 (overlapping m, COD-C*H*).

[(dppm)Rh(dppm-H)] (4). A solution of **1** (0.04 g, 0.06 mmol) in benzene (2 mL) was treated with an excess of dppm (0.12 g, 0.30 mmol). Upon warming to 50 °C for 2 min, the initially yellow solution became red, and upon slow cooling, deep-red crystals of the sparingly soluble product were obtained. Yield = 0.10 g (93%). Due to the fact that the crystals obtained contained 2 benzene molecules per Rh and underwent partial solvent loss upon drying, satisfactory elemental analysis was not possible. ^{1}H NMR (C_6D_6, 30 °C): δ 3.34 [br, C*H*(PPh$_2$)$_2$], 4.08 [t, C*H*$_2$(PPh$_2$)$_2$], 6.8–7.9 (m, aromatics). ^{31}P NMR (C_6D_6, 30 °C): δ −25.8, −20.4 (AA′BB′X patterns due to ^{31}P nuclei of dppm and dppm ligands).

[(dppm)Ir(dppm-H)] (5). An essentially identical procedure to that used for **4** above only heating the mixture at 80 °C for minutes led to the formation of very sparingly soluble **5**. ^{1}H NMR (C_6D_6, 30 °C): δ 3.68 [br, C*H*(PPh$_2$)$_2$], 4.71 [t, C*H*$_2$(PPh$_2$)$_2$], 6.7–7.0 (m, aromatics).

Crystallographic Studies. Crystal data and data collection parameters for compounds **1**–**4** are contained in Table IV. Further details of the crystallographic study are contained in the supplementary material.

Acknowledgment. We thank the National Science Foundation (Grant CHE-8915573) for support of this research.

Supplementary Material Available: Tables of fractional coordinates, thermal parameters, and full bond distances and angles for **1**–**4** (43 pages); tables of observed and calculated structure factors for **1**–**4** (91 pages). Ordering information is given on any current masthead page.

Alkylidene-Transfer Processes in the Reactions of Cp$_2$Ta(=CH$_2$)(CH$_3$) with Silanes

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Received May 7, 1990

$Cp_2Ta({=}CH_2)(Me)$ (**1**; Cp ≡ η^5-C_5H_5) reacts with relatively unhindered silanes such as Me_2SiH_2 and Me_3SiH in tetrahydrofuran (THF) or benzene to produce equal amounts of $Cp_2Ta(H_2C{=}CH_2)(Me)$ and the bis(silyl) complexes $Cp_2Ta(SiR_3)_2(H)$ (SiR_3 = $SiMe_2H$, $SiMe_3$) with concurrent liberation of methane. The reaction mechanism involves rate-limiting disproportionation of **1** to $Cp_2Ta(H_2C{=}CH_2)(Me)$ and the unsaturated intermediate $Cp_2Ta(Me)$, which subsequently reacts with silanes to yield the bis(silyl) complexes. In contrast, **1** reacts with the hindered silane $H_2Si(t\text{-}Bu)_2$ in THF to yield the silyl-substituted alkylidene hydride complex $Cp_2Ta(H)({=}C(H)(SiH(t\text{-}Bu)_2))$ (**2**) and varying amounts of the bridging alkylidene complex $\{CpTa(\mu_2\text{-}\eta^1{:}\eta^5\text{-}C_5H_4)\}_2(\mu\text{-}C(H)(SiH(t\text{-}Bu)_2))$ (**3**). In this instance, the reaction proceeds by a novel chain mechanism involving alkylidene transfer between tantalum centers in which the key chain-carrying species is the unsaturated intermediate $Cp_2Ta(Me)$. Reversible hydrogen transfer from tantalum to the alkylidene carbon in **2** is facile, and the resultant unsaturated alkyl can be readily trapped by donor ligands to produce $Cp_2Ta(L)(CH_2SiH(t\text{-}Bu)_2)$ (**4a**,**b**; L = CO, PMe$_3$). The reaction of **1** with $H_2Si(t\text{-}Bu)_2$ in benzene also produces the phenyl methylene complex $Cp_2Ta({=}CH_2)(Ph)$ (**5**) in addition to **2**, as a result of competing benzene C–H activation during the reaction. Finally, the order of relative rates for ligand to alkylidene migratory insertion in complexes of the type $Cp_2Ta({=}CHR)(X)$ is observed to be $X = H > SiH(t\text{-}Bu)_2 \gg Ph > Me$. Compounds **3** and **4a** have been structurally characterized by single-crystal X-ray diffraction methods (**3**, triclinic, $P\bar{1}$, $Z = 2$, $a = 8.001$ (1) Å, $b = 10.389$ (1) Å, $c = 13.747$ (2) Å, $\alpha = 68.80$ (1)°, $\beta = 78.49$ (1)°, $\gamma = 76.97$ (1)°, $V = 1029.1$ Å^3; **4a**, monoclinic, $C2/c$, $Z = 8$, $a = 30.922$ (4) Å, $b = 8.094$ (2) Å, $c = 20.517$ (3) Å, $\beta = 96.15$ (1)°, $V = 5105.2$ Å^3).

Introduction

Many important reactions of transition-metal carbene and alkylidene complexes involve the net transfer of a carbene fragment to an unsaturated substrate. Common examples utilizing organic substrates include cyclopropanation of olefins,[2] olefin metathesis,[3] conversion of

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