attempts to trace the resulting organic product are yet unsuccessful.[17]

In summary, we find it significant that at an originally electronically saturated metal cluster complex, both the oxidative cleavage of a P–C bond and the subsequent migration of the organic group can be made to occur at very mild conditions, in contrast to the stability of diphenylpyridylphosphine toward $Ru_3(CO)_{12}$ in thermally induced substitution reactions.[4]

Acknowledgment. Financial support from the CNRS is gratefully acknowledged. We also thank Johnson Matthey for a generous loan of $RuCl_3$.

Supplementary Material Available: Listings of crystal and intensity data, positional and thermal parameters, and selected interatomic distances and bond angles for complex **2** (Tables I–V) and complex **3** (Tables VI–X) (18 pages). Ordering information is given on any current masthead page.

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Received October 1, 1985

(17) Analysis by GC gave no evidence for any of the following products: benzene, benzaldehyde, benzyl alcohol, diphenylglyoxal.

Articles

Contribution from the Department of Chemistry, Tulane University, New Orleans, Louisiana 70118

Synthesis of New Hybrid Phosphine Amide Complexes of Rhodium(I) and Iridium(I). Intramolecular "Chelate-Assisted" Oxidative Addition of an N–H Bond to Iridium(I)

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The hybrid phosphine amide ligands *o*-$Ph_2PC_6H_4NHC(O)Ph$ (PNH(CPhO)) and *o*-$Ph_2PC_6H_4C(O)NHPh$ (P(CO)NHPh)) react with $[MCl(1,5\text{-COD})]_2$ to give the monomeric complexes MCl(1,5-COD)PNH(CPhO)) and MCl(1,5-COD)(P(CO)NHPh) (M = Rh, Ir). The complexes are 4-coordinate with a P-bonded monodentate phosphine amide ligand. P,N-Chelate complexes $[M(1,5\text{-COD})(PN(CPh(OH)))]ClO_4$ and $[M(1,5\text{-COD})(P(COH)NPh)]ClO_4$ (M = Rh, Ir) are formed by the addition of 1 equiv of the ligand to $[M(1,5\text{-COD})(THF)_2]ClO_4$. The complexes are proposed to have the hybrid ligand coordinated through a nitrogen in the iminoyl form. Solutions of the complexes in acetonitrile solvent undergo intramolecular exchange. For $[Rh(1,5\text{-COD})(PN(CPh(OH)))]^+$ this pathway involves replacement of the iminoyl by MeCN, but for $[Rh(1,5\text{-COD})(P(COH)NPh)]^+$ the process involves addition of MeCN into the fifth coordination position. In the case where iminoyl substitution occurs, the dangling ligand arm has the amide structure. The complexes RhCl(1,5-COD)(PNH(CPhO)), RhCl(1,5-COD)(P(CO)NHPh), and IrCl(1,5-COD)(P(CO)NHPh) react with base to give respectively Rh(1,5-COD)(PN(CPhO)), Rh(1,5-COD)(P(CO)NPh), and Ir(1,5-COD)(P(CO)NPh).

Recently we have synthesized some new hybrid phosphine amide ligands in order to induce N–H addition to a low-valent transition-metal center. The compounds can form chelate complexes having either 5- or 6-membered rings, and we anticipated that the insertion of the metal center into the N–H bond would be intramolecularly facilitated by chelation to the phosphorus anchor.[1] Following a preliminary communication,[2] we have published two articles describing the synthesis of the hybrid ligands, along with the chemistry of the palladium(II) and platinum(II) complexes.[3,4] In these first two papers we reported the synthesis of P-bonded monodentate Pd(II) and Pt(II) complexes of the phosphine amides, and we described the reactions of these complexes with added bases and acids in order to reversibly convert the compounds to chelated phosphine amido complexes. Thermolysis yielded cyclometalated products, and a platinum(II) complex was characterized having a monodentate P-bonded phosphine amide ligand with an "agostic" N–H bond. With these palladium(II) and platinum(II) complexes no metal hydrides were observed, nor were complexes having a protonated amide ligand bonded to the metal ionn. Complexes of rhodium(I) and iridium(I) are more reactive to oxidative addition than their d^8 congeners of palladium(II) and platinum(II), and furthermore for amide chelation these metal centers are more susceptible to achieving pentacoordination.[5]

This article describes the reaction chemistry of our phosphine amide ligands with chloro-bridged rhodium(I) and iridium(I) alkene complexes. The particular ligands used are *o*-$Ph_2PC_6H_4NHC(O)Ph$ (PNH(CPhO)) and *o*-$Ph_2PC_6H_4C(O)NHPh$ (P(CO)NHPh) (Figure 1).[3] The former compound can be used to prepare 5-membered ring chelate complexes, and the latter the analogous 6-membered ring complexes. Deprotonation of the coordinated amide nitrogen can be used to synthesize the corresponding amido complexes. In this paper we describe the synthesis and reaction chemistry of new chelate complexes having both the phosphorus atom and the uncharged amide nitrogen complexed to rhodium(I) and iridium(I). In addition to these d^8 complexes we also describe the synthesis of the first amido hydride complexes of iridium(III), which have been formed by the oxidative addition of the amide N–H bond to iridium(I).

Experimental Section

Many of the experimental details have been described in the two earlier papers.[3,4] The air-sensitive complexes prepared in this paper have been handled by Schlenk techniques or in a Vacuum Atmospheres drybox. Our Schlenk techniques use a standard double-manifold setup and single-side-arm Schlenk vessels. Liquid transfer is effected by stainless-steel transfer tubes through Suba Seal septa (Strem). NMR spectra of air-sensitive complexes were measured in 10-mm septum-capped tubes (Wilmad Co.). Rhodium trichloride and iridium trichloride were sup-

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0020-1669/86/1325-0009$01.50/0

PNH(CPhO) P(CO)NHPh

Figure 1. Structures of PNH(CPhO) and P(CO)NHPh.

plied by Engelhard Industries and Matthey Bishop Corp. ^{1}H NMR Spectra in the upfield hydride region were measured on a JEOL FX90Q spectrometer operating at 90 MHz. Infrared spectra were measured with the samples prepared as Nujol mulls or as solutions in matched IR cells. In the tabulated data we identify the medium used. The compounds PNH(CPhO) and P(CO)NHPh, and the complexes $[RhCl(1,5\text{-}COD)]_2$, $[IrCl(1,5\text{-}COD)]_2$, and $[IrCl(C_8H_{14})_2]_2$ were prepared as previously described.[6] 1,4-Diazabicyclo[2.2.2]octane (Dabco) was purchased from Aldrich.

RhCl(1,5-COD)(PNH(CPhO)) (1). A solution of $[RhCl(1,5\text{-}COD)]_2$ (313 mg, 0.64 mmol) in N_2-saturated dichloromethane (5 mL) was treated with a solution of PNH(CPhO) (484 mg, 1.28 mmol) in the same solvent. After the orange solution was stirred for 30 min, the solvent volume was reduced to 5 mL and cyclohexane (40 mL) added. Vacuum filtration gave the complex as a pale yellow crystalline solid. The compound was washed with diethyl ether (10 mL) and dried in vacuo: yield 687 mg (87%); mp 198–200 °C dec. Anal. Calcd for $C_{33}H_{32}ClNOPRh$: C, 63.1; H, 5.14; P, 4.93. Found: C, 64.0; H, 5.36; P, 4.93. Λ_M(0.81 mM in CH_3CN) = 1.4 Ω^{-1} cm^2 mol^{-1}.

RhCl(1,5-COD)(P(CO)NHPh) (2). Using a similar procedure as for **1** with $[RhCl(1,5\text{-}COD)]_2$ (310 mg, 0.63 mmol) and P(CO)NHPh (480 mg, 1.26 mmol) gave complex **2** as a yellow powder: yield 705 mg (89%); *mp 200–202* °C dec. Anal. Calcd for $C_{33}H_{32}ClNOPRh$: C, 63.1; H, 5.14; P, 4.93. Found: C, 63.1; H, 5.26; P, 4.77. Λ_M(0.85 mM in CH_3CN) = 7.4 Ω^{-1} cm^2 mol^{-1}.

IrCl(1,5-COD)(PNH(CPhO)) (3). By the use of a procedure similar to that used to prepare **1**, except that hexane (75 mL) was used instead of cyclohexane, the compound $[IrCl(1,5\text{-}COD)]_2$ (200 mg, 0.30 mmol) and PNH(CPhO) (228 mg, 0.60 mmol) gave complex **3** as a light orange powder: yield 370 mg (86%); mp 132–134 °C. Anal. Calcd for $C_{33}H_{32}ClIrNOP$: C, 55.3; H, 4.50; P, 4.32. Found: C, 55.3; H, 4.86; P, 4.04. Λ_M(0.74 mM in CH_3CN) = 5.1 Ω^{-1} cm^2 mol^{-1}.

IrCl(1,5-COD)(P(CO)NHPh) (4). Using an analogous procedure as for **3** with $[IrCl(1,5\text{-}COD)]_2$ (200 mg, 0.30 mmol) and P(CO)NHPh (228 mg, 0.60 mmol) gave complex **4** as a light orange powder: yield 358 mg (83%); mp darkness from 160 to 300 °C. Anal. Calcd for $C_{33}H_{32}ClIrNOP$: C, 55.3; H, 4.50; P, 4.32. Found: C, 54.9; H, 4.42; P, 4.02. Λ_M(0.67 mM in CH_3CN) = 8.8 Ω^{-1} cm^2 mol^{-1}.

[Rh(1,5-COD)(PN(CPh(OH)))]ClO$_4$ (5). The complex $[RhCl(1,5\text{-}COD)]_2$ (100 mg, 0.20 mmol) and $AgClO_4$ (84 mg, 0.40 mmol) were placed in a Schlenk vessel fitted with a filter assembly and equipped with a magnetic stir bar. The flask was purged on the double-manifold Schlenk line. Dry oxygen-free THF (5 mL) was added, and the mixure was stirred for 20 min. The THF solution of $[Rh(1,5\text{-}COD)(THF)_2]ClO_4$ was filtered into a N_2-fitted Schlenk vessel to remove the precipitated AgCl. A solution of PNH(CPhO) (155 mg, 0.40 mmol) in dry oxygen-free THF (5 mL) was transferred to the yellow solution of $[Rh(1,5\text{-}COD)(THF)_2]ClO_4$. An immediate color change to light orange was observed. The solvent was removed after stirring for 20 min, and the solids were redissolved in nitrogen-saturated dichloromethane (5 mL). The suspension was gravity-filtered under nitrogen, and nitrogen-saturated hexane (40 mL) was added dropwise to precipitate the product as a yellow powder. The complex was isolated by vacuum filtration under nitrogen and dried in vacuo; yield 252 mg (89%). The complex was too thermally unstable for microanalysis, even in vacuum-sealed samples.

[Rh(1,5-COD)(P(COH)NPh)]ClO$_4$ (6). By the use of a procedure analogous to that used to prepare **5**, with $[RhCl(1,5\text{-}COD)]_2$ (88 mg, 0.18 mmol), $AgClO_4$ (74 mg, 0.36 mmol), and P(CO)NHPh (135 mg, 0.36 mmol), the complex was obtained as a thermally unstable bright yellow powder, yield 170 mg (69%).

[Ir(1,5-COD)(PN(CPh(OH)))]ClO$_4$ (7) and [Ir(1,5-COD)(P(COH)-NPh)]ClO$_4$ (8). The complex $[Ir(1,5\text{-}COD)(THF)_2]ClO_4$ was prepared from $[IrCl(1,5\text{-}COD)]_2$ (100 mg, 0.15 mmol) and $AgClO_4$ (62 mg, 0.30 mmol) as described for the synthesis of $[Rh(1,5\text{-}COD)(THF)_2]ClO_4$. Use of a procedure as for **5** with PNH(CPhO) or P(CO)NHPh (114 mg, 0.30 mmol) gave the complexes as thermally unstable light orange powders. Yields were approximately 170 mg.

Rh(1,5-COD)(PN(CPhO))·CH$_2$Cl$_2$ (9). Complex **1** (200 mg, 0.32 mmol) was suspended in nitrogen-saturated acetonitrile (20 mL). Excess Dabco (200 mg, 1.8 mmol) and sodium carbonate (40 mg) were added to the yellow suspension. The mixture was stirred under N_2 for 3 h, during which time there was a conversion to a light orange solution. Solvent removal gave an orange residue, which was redissolved in dichloromethane (10 mL). This solution was extracted with deionized water (3 × 20 mL), and the organic layer was dried over anhydrous $MgSO_4$. The dried solution was vacuum-filtered, and after addition of hexane (50 mL), the complex precipitated as a pale yellow powder. The final product was isolated by vacuum filtration and dried in vacuo; yield 145 mg (77%). Anal. Calcd for $C_{34}H_{33}Cl_2NOPRh$: C, 60.4; H, 4.92. Found, C, 60.5; H, 5.00. Λ_M(0.89 mM in CH_3CN) = 3.3 Ω^{-1} cm^2 mol^{-1}. The complex must be stored in an evacuated glass ampule.

Rh(1,5-COD)(P(CO)NPh)·CH$_2$Cl$_2$ (10). Using an analogous procedure as for **9**, with **2** (200 mg, 0.32 mmol), gave complex **10** as a pale yellow powder, yield 140 mg (75%). Anal. Calcd for $C_{34}H_{33}Cl_2NOPRh$: C, 60.4; H, 4.92. Found: C, 60.6; H, 4.82. Λ_M(0.93 mM in CH_3CN) = 0.97 Ω^{-1} cm^2 mol^{-1}.

Ir(1,5-COD)(P(CO)NPh) (11). Complex **4** (100 mg, 0.14 mmol) and excess Dabco (100 mg, 0.90 mmol) were dissolved in nitrogen-saturated dichloromethane (30 mL). The solution was stirred under nitrogen for 60 min, during which time the solution color changed from light yellow to orange. The solution was extracted with 10% aqueous sodium chloride (4 × 40 mL), and the organic layer was separated and dried over anhydrous $MgSO_4$. The solution was filtered, the volume reduced to ca. 2 mL and hexane (80 mL) added to precipitate the complex as a bright orange powder. The product was isolated by vacuum filtration, washed with hexane, and dried in vacuo; yield 72 mg (78%). Anal. Calcd for $C_{33}H_{31}IrNOP$: C, 58.2; H, 4.59. Found: C, 57.2; H, 4.54.

IrHCl(PN(CPhO))(PPh$_3$)$_2$ (12a,b). $[IrCl(C_8H_{14})]_2$ (50 mg, 0.056 mmol) was placed in a Schlenk vessel equipped with a magnetic stir bar and fitted with a filter assembly. The vessel was purged with dry nitrogen on the Schlenk line. Dry oxygen-free toluene (5 mL) was transferred to the vessel, and the suspension was vigorously stirred. A solution of triphenylphosphine (58 mg, 0.22 mmol) in dry oxygen-free toluene (5 mL) was transferred to the suspension, and the mixture was stirred for 5 min to give a dark red-orange solution. A solution of PNH(CPhO) (43 mg, 0.11 mmol) in dry oxygen-free toluene (5 mL) was then added to the red-orange solution. After 2 h of stirring, the color of the solution changed to pale yellow. Filtration removed metallic iridium, and the volume of the solution was reduced to ca. 2 mL. Addition of oxygen-free hexane (40 mL) precipitated the product as a pale yellow powder. The computer was washed well with hexane (5 × 20 mL) to remove traces of cyclooctene and then dried in vacuo; yield 85 mg (67%). Anal. Calcd for $C_{61}H_{50}ClIrNOP_3$: C, 64.6; H, 4.45; P, 8.20. Found: C, 64.8; H, 4.63; P, 7.30. Λ_M(0.98 mM in CH_3CN) = 8.8 Ω^{-1} cm^2 mol^{-1}.

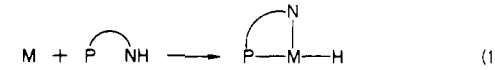
IrHCl(PN(CPhO))dppe (13a,b). By the use of a procedure analogous to that used to prepare **12**, with $[IrCl(C_8H_{14})_2]_2$ (50 mg, 0.56 mmol), dppe (44 mg, 0.12 mmol), and PNH(CPhO) (43 mg, 0.12 mmol), the complex was isolated as a pale yellow powder. Anal. Calcd for $C_{51}H_{44}ClIrNOP_3$: C, 60.8; H, 4.40; Cl, 3.52; P, 9.22. Found: C, 61.0; H, 4.55; Cl, 2.93; P, 8.66. Λ_M(1.01 mM in CH_3CN) = 8.0 Ω^{-1} cm^2 mol^{-1}.

IrHCl(PN(CPhO))(AsPh$_3$)$_2$ (14a,b). Complex **14** was prepared from $[IrCl(C_8H_{14})]_2$ (50 mg, 0.056 mmol), $AsPh_3$ (69 mg, 0.24 mmol), and PNH(CPhO) (43 mg, 0.12 mmol) using a procedure analogous to that used for complex **12**. The complex was isolated as a pale orange powder. Anal. Calcd for $C_{61}H_{54}As_2ClIrNOP$: C, 59.8; H, 4.44. Found: C, 60.0; H, 4.46.

IrHCl(PN(CPhO))(1,5-COD) (15). Complex **3** (50 mg, 0.07 mmol) was reacted as described in the synthesis of **11** from **4** to give **15** as a pale orange solid, yield 35 mg (73%).

Results and Discussion

This paper, the third in our series with these phosphine amide hybrid ligands, focuses on achieving our goal of intramolecular insertion of a transition-metal center into an N–H bond. Strategically we can accomplish this goal if we can use as metal center a complex that has three coordination sites available for complexation and that can also readily undergo a two-electron oxidative addition (eq 1). Two groups of complexes appear to fulfill



(1)

these criteria; these are transition-metal complexes having either a d^8 or a d^{10} electron configuration. Since elements in the third transition series undergo the most facile oxidation, the complexes of choice would be those having Ir(I) or Pt(0) centers. This paper

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Table I. ^1H and $^{31}P\{^1H\}$ NMR Spectral Data for New Phosphine Amide Complexes of Rhodium and Iridium

no.	complex	δ(P)[a]	δ(H)[a]
1	RhCl(1,5-COD)(PNH(CPhO))	13.6 d (^1J = 145)	10.4 (NH, 1 H), 8.3–6.7 (Ph, 19 H), 5.4 (CH, 2 H), 3.1 (CH, 2 H), 2.1–1.5 (CH_2, 8 H)
2	RhCl(1,5-COD)(P(CO)NHPh)	21.9 d (^1J = 148)	8.4 (NH, 1 H), 8.0–7.0 (Ph, 19 H), 5.1 (CH, 2 H), 3.6 (CH, 2 H), 1.4–2.1 (CH_2, 8 H)
3	IrCl(1,5-COD)(PNH(CPhO))	6.7 s	10.0 (NH, 1 H), 8.1–6.7 (Ph, 19 H), 5.2 (CH, 2 H), 2.7 (CH, 2 H), 2.1–1.5 (CH_2, 8 H)
4	IrCl(1,5-COD)(P(CO)NHPh)	14.4 s	8.3 (NH, 1 H), 8.0–7.0 (Ph, 19 H), 4.8 (CH, 2 H), 3.2 (CH, 2 H), 2.0–1.5 (CH_2, 8 H)
5	$[Rh(1,5\text{-}COD)(PN(CPh(OH)))]ClO_4$	18.4 d (^1J = 144)	9.7 (OH, 1 H), 6.9–7.8 (Ph, 19 H), 5.2 (CH, 2 H), 3.4 (CH, 2 H), 2.0–1.4 (CH_2, 8 H)
6	$[Rh(1,5\text{-}COD)(P(COH)NPh)]ClO_4$	23.4 d (^1J = 148)	9.8 (OH, 1 H), 7.0–8.2 (Ph, 19 H), 5.3 (CH, 2 H), 3.4 (CH, 2 H), 2.3–1.7 (CH_2, 8 H)
7	$[Ir(1,5\text{-}COD)(PN(CPh(OH)))]ClO_4$		7.0–8.0 (Ph, 19 H), 4.9 (CH, 2 H), 3.9 (CH, 2 H), 2.2–1.8 (CH_2, 8 H)
8	$[Ir(1,5\text{-}COD)(P(COH)NPh)]ClO_4$		7.0–8.0 (Ph, 19 H), 4.9 (CH, 2 H), 3.9 (CH, 2 H), 2.2–1.8 (CH_2, 8 H)
9	Rh(1,5-COD)(PN(CPhO))	35.6 d (^1J = 160)	6.5–8.0 (Ph, 19 H), 5.5 (CH, 2 H), 3.3 (CH, 2 H), 2.2–1.9 (CH_2, 8 H)
10	Rh(1,5-COD)(P(CO)NPh)	25.1 d (^1J = 156)	6.5–8.0 (Ph, 19 H), 4.4 (CH, 2 H), 3.3 (CH, 2 H), 2.3–1.7 (CH_2, 8 H)
11	Ir(1,5-COD)(P(CO)NPh)	8.8	6.6–8.2 (Ph, 19 H), 4.2 (CH, 2 H), 2.7 (CH, 2 H), 2.2–1.4 (CH_2, 8 H)
12a	$IrHCl(PN(CPhO))(PPh_3)_2$ (major)	6.0, −6.0, −7.9	−17.9 (IrH, ddd, J = 19,10,9)
12b	$IrHCl(PN(CPhO))(PPh_3)_2$	multiplets	−17.2 (IrH, dt, J = 364,16)
13a	IrHCl(PN(CPhO))dppe (major)	multiplets	−19.7 (IrH, ddd, J = 26,14,12)
13b	IrHCl(PN(CPhO))dppe	multiplets	−20.1 (IrH, dt, J = 194,12)
14a	$IrHCl(PN(CPhO))(AsPh_3)_2$ (major)	8.2	−15.6 (IrH, d, J = 13)
14b	$IrHCl(PN(CPhO))(AsPh_3)_2$	7.6	−16.6 (IrH, d, J = 10)
15	IrHCl(1,5-COD)(PN(CPhO))	15.4	8.3–6.8 (Ph, 19 H), 4.4 (CH, 2 H), 3.9 (CH, 2 H), 2.1–1.5 (CH_2, 8 H)

[a] All J values are in Hz.

Table II. IR spectral Data (cm^{-1}) for New Phosphine Amide Complexes of Rhodium and Iridium

complex	ν(NH), ν(OH)	ν(IrH)	amide I	amide II	amide III	$\nu_{asym}(ClO_4^-)$
PNH(CPhO)	3350	...	1680	1510	1300	
P(CO)NHPh	3240	...	1650	1550	1330	
1	3260 (NH)	...	1670	1500	1295	...
2	3320 (NH)	...	1660	1540	1320	...
3	3200 (NH)	...	1675	1500	1295	...
4	3340 (NH)	...	1665, 1650	1540	1320	...
5	3260 (OH)	...	1605 (C=N)	1540	1335	1110
6	3300 (OH)	...	1610 (C=N)	1550	1340	1110
7	3400 (OH) 3200 (OH)	...	1690, 1610 (C=N)			1110
8	3300 (OH)	...	1660, 1610 (C=N)			1110
9	...	...	1600	...	1310	...
10	...	...	1600	...	1360	...
11		...	1600	...	1330	...
12a	...	2220	1595	...	1360	...
12b	...	2040	1595	...	1360	...
13a	...	2220	1590	...	1335	...
13b	...	2040	1590	...	1335	...
14a	...	2200	1595	...	1320	...
14b	...	2040	1595	...	1320	...
15	...	2160, 2140	1610	...	1330	...

reports our results with iridium(I) and rhodium(I) complexes and also shows how we can isolate hydride complexes by the N–H addition to iridium(I).

Rhodium(I) and Iridium(I) Complexes. As shown in eq 1 our strategy is to use a metal center that has three available coordination sites. Such a condition is fulfilled with the 4-coordinate bridged complexes $[M(\mu\text{-}Cl)(1,5\text{-}COD)]_2$ (M = Rh, Ir). Since halide bridge cleavage by added tertiary phosphine is a well-documented reaction, we anticipate that such a bridge cleavage will be the first step upon addition of a hybrid phosphine amide ligand to $[M(\mu\text{-}Cl)(1,5\text{-}COD)]_2$. The monomeric tetracoordinate P-bonded complex so formed can then potentially add the N–H bond from the uncoordinated amide functionality. Our premise that bridge cleavage will be the initial step has been verified by the formation of MCl(1,5-COD)(PNH(CPhO)) and MCl(1,5-COD)(P(CO)NHPh) (M = Rh, Ir) from the respective reactions of PNH(CPhO) and P(CO)NHPh with $[M(\mu\text{-}Cl)(1,5\text{-}COD)]_2$ (eq 2). This method has been used to prepare complexes **1–4**.

$$\tfrac{1}{2}[M(\mu\text{-}Cl)(1,5\text{-}CO)]_2 + P\frown NH \rightarrow MCl(1,5\text{-}COD)(P\frown NH) \quad (2)$$

M = Rh, Ir; P⌒NH = PNH(CPhO), P(CO)NHPh

The complexes have d^8 rhodium(I) and iridium(I) metal centers.

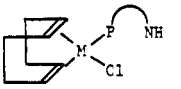


Figure 2. Structures of complexes **1–4** (P⌒NH = PNH(CPhO), M = Rh (**1**), Ir (**2**); P⌒NH = P(CO)NHPh, M = Rh (**3**), Ir (**4**)).

Intramolecular insertion into the N–H bond does not occur, although the analogous complexes with $o\text{-}Ph_2PC_6H_4CHO$ in place of PNH(CPhO) or P(CO)NHPh have previously been found to undergo intramolecular C–H addition.[1] The spectroscopic properties of this group of new complexes (**1–4**) are closely similar (Tables I and II). Structurally these complexes are 4-coordinate with a monodentate P-bonded P⌒NH ligand (Figure 2). The free uncoordinated hybrid phosphine amide compounds are characterized by the following spectroscopic parameters: for PNH(CPhO) δ(P) = −26.8, δ(NH) = 8.80, ν(NH) = 3350 cm^{-1}, amide I = 1680 cm^{-1}, amide II = 1510 cm^{-1}, and amide III = 1300 cm^{-1}; for P(CO)NHPh δ(P) = −16.4, δ(NH) = 3240 cm^{-1}, amide I = 1650 cm^{-1}, amide II = 1550 cm^{-1}, and amide III = 1330 cm^{-1}.

The $^{31}P\{^1H\}$ NMR spectra of this group of complexes show the presence of a single phosphorus atom complexed to rhodium(I) or iridium(I). The resonances are downfield shifted some 30–40

ppm from the free ligand positions of the resonances. The magnitude of ^1J(RhP) is typical for a rhodium(I)-complexed monodentate phosphine ligand.[7]

In the ^{1}H NMR spectra of complexes **1–4** the methylene hydrogens in the coordinated 1,5-cyclooctadiene ligand appear as a broad multiplet between 1.5 and 2.0 ppm. The olefinic hydrogens are also unresolved and are found at δ = ca. 3.0 for the alkene trans to Cl and at δ = ca. 5.0 for the alkene cis to Cl. The multiplicity of the peaks is due to coupling between H–H, H–P, and H–Rh. The resonances due to δ(NH) are downfield shifted by some 1.2 ppm from the free ligand position in PNH(CPhO). For complexes **2** and **4** the respective values of δ(NH) are 8.4 and 8.3; however, since the resonance due to δ(NH) in P(CO)NHPh itself is uobserved, we cannot assess differences that occur upon coordination to rhodium(I) or iridium(I).

The IR spectra correlate with the NMR spectra. For complexes **1** and **3** we find ν(NH) at 3260 and 3200 cm^{-1} respectively, and for complexes **2** and **4** the respective values are 3320 and 3340 cm^{-1}. For the former pair, the shift in ν(NH) is some 90–150 cm^{-1} to lower energy, but for the latter pair the shift is only some 80–100 cm^{-1}, but now the shift is to higher energy. The reluctance of these low-valent d^8 complexes to undergo N–H oxidative addition may be a consequence of the presence of the electron-withdrawing 1,5-cyclooctadiene ligand, or it may be due to the absence of any intramolecular interaction between the amide group and the metal center on the pathway to insertion. Both hypotheses are testable.

Removal of a chloride ion from complexes **1–4** will create a 14-electron intermediate, which can be expected to readily form an intramolecular chelate complex by coordination to the hinged amide group (eq 3). Treating complexes **1–4** with the halide-

$$MCl(1,5\text{-}COD)(P\frown NH) \rightarrow M(1,5\text{-}COD)(P\frown NH)^+ + Cl^- \quad (3)$$

abstracting agents $AgClO_4$ or $NaBPh_4$ in a coordinating solvent is a conceptually feasible approach. Alternatively the 4-coordinate d^8 complexes can be prepared from the reaction of PNH(CPhO) or P(CO)NHPh with the complexes $[M(1,5\text{-}COD)(THF)_2]ClO_4$. This latter method has been found to be the preferred one. The cationic THF complexes are prepared by standard procedures[8] in oxygen-free THF. To these complexes in situ is added 1 equiv of P$\frown$NH (P$\frown$NH = PNH(CPhO), P(CO)NHPh) under Schlenk conditions. The chelate ligands substitute THF under ambient conditions to yield the 4-coordinate d^8 complexes $[M(1,5\text{-}COD)(P\frown NH)]ClO_4$ (M = Rh, Ir) (eq 4). The complexes are

$$[M(1,5\text{-}COD)(THF)_2]ClO_4 + P\frown NH \rightarrow [M(1,5\text{-}COD)(P\frown NH)]ClO_4 + 2THF \quad (4)$$

M = Rh; P$\frown$NH = PNH(CPhO) (**5**), P(CO)NHPh (**6**)

M = Ir; P$\frown$NH = PNH(CPhO) (**7**), P(CO)NHPh (**8**)

obtained as yellow powders, which are oxygen sensitive both in the solid and the solution states. The complexes are soluble in polar organic solvents. The rhodium complexes have a somewhat higher solution stability, and therefore we have made more detailed studies on this pair of complexes. Neither set of complexes show any tendency to undergo intramolecular N–H oxidative addition.

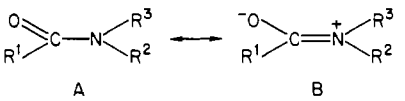
The solid-state infrared spectra (Nujol) of complexes **5** and **6** show significant changes from that of free ligand. The amide I bands are shifted to lower frequency by some 60 cm^{-1} from their position in the free ligand, and the amide II and III bands are shifted to higher frequency. The spectra show a broad band in the 3300-cm^{-1} region, which verifies that the coordinated ligand remains protonated. The solution-state infrared spectra (CH_2Cl_2) are identical except for a very slight shift in the 3300 cm^{-1} band. The observation of a band in the infrared spectrum at 3300 cm^{-1} and a shift in the amide I band to the 1600-cm^{-1} region show that the amide group is coordinated as a chelate ligand. The amide

A B

Figure 3. Possible stereochemistry of complex **12a** (L = PPh_3).

II bands are found at 1540 cm^{-1} (**5**) and 1550 cm^{-1} (**6**), whereas the corresponding amide III bands are at 1335 cm^{-1} (**5**) and 1340 cm^{-1} (**6**).[9]

Three different coordination modes for the amido end of the hybrid ligand are feasible. These are (i) coordination of the amide nitrogen via the lone electron pair, (ii) coordination via the amide oxygen atom, or (iii) coordination via the nitrogen of the iminol tautomer. The first possibility is unlikely from our data; we expect coordination via amide nitrogen will diminish the contribution of the dipolar resonance form B in (5). As a consequence we expect

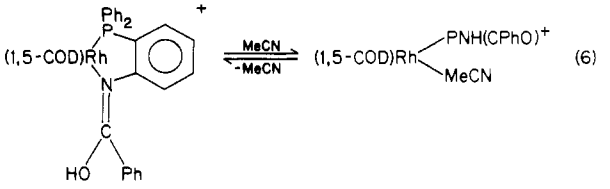


A B (5)

an increase in the frequency of the amide I band from the free ligand position. We observe a decrease in this amide I band in complexes **5–8**. Options ii and iii are feasible, and discrimination between these coordination modes is not easy. Furthermore we cannot discount the possibility that we have a π-complex, but we believe that the high frequency of the amide I band makes this unlikely. The IR spectral data for **5-8** are closely similar, which indicates that the mode of spectral bonding is consistent within the group of complexes. We propose that the amide group is N-bonded via the iminol tautomer (iii). The structures are shown in Figure 3. This coordination mode gives 5- and 6-membered ring complexes with PNH(CPhO) and P(CO)NHPh respectively, but coordination via oxygen results in chelate complexes with 7- and 6-membered rings with these ligands. Formation of a 7-membered ring with a weakly bonded ketonic oxygen in chelation is a rather unlikely possibility. We therefore assign the bands in the 3300-cm^{-1} region to ν(OH), and those in the 1600-cm^{-1} region to ν(C=N). These found values for **5–8** correlate with the corresponding stretching frequencies observed in other complexed iminoyl groups.[10]

Complexes **5** and **6** show the respective molar conductivities of 21.9 Ω^{-1} cm^2 mol^{-1} (0.94 mM solutions in CH_2Cl_2) and 23.3 Ω^{-1} cm^2 mol^{-1} (0.89 mM solution in CH_2Cl_2). These values are significantly lower than the value of 51.7 Ω^{-1} cm^2 mol^{-1} (1.0 mM solution in CH_2Cl_2) found for $[Rh(1,5\text{-}COD)(dppe)]ClO_4$. These lowered values for **5** and **6** are likely due to ion pairing. The ^{31}P NMR chemical shifts for **5** and **6** show very small ring shift effects due to chelation (Δ_R = δ 4.8 and 1.5), and ^1J(RhP) values are the same as for **1** and **2**. The ^{1}H NMR spectra show a rather sharp resonance due to δ(OH) at 9.8, which is invariant over the temperature range of 27 to −60 °C.

The iminol arm of the chelate ligand in complex **5** is replaced by acetonitrile (eq 6). The ^{1}H NMR spectrum of **5** upon addition

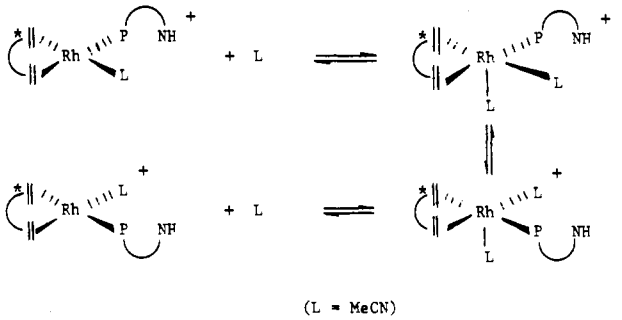


(6)

of acetonitrile shows the disappearance of the olefinic (1,5-COD) resonances and the growth of a new peak at δ 4.5. The OH

(7) Pregosin, P. S.; Kunz, R. W. "^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes"; Springer-Verlag: New York, 1979.
(8) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 2134–2143.
(9) Challis, B. C.; Challis, J. A. In "Comprehensive Organic Chemistry"; Barton, D., Ollis, W. D., Sutherland, I. O., Eds; Pergamon Press: Oxford, England, 1979; Vol. 2, pp 990–994.
(10) Brown, D. B.; Burbank, R. D.; Robin, M. B. *J. Am. Chem. Soc.* **1969**, *91*, 2895–2902. Bellamy, L. J. "The Infrared Spectra of Complex Molecules", 3rd ed.; Chapman & Hall: London, 1975; pp 294–303.

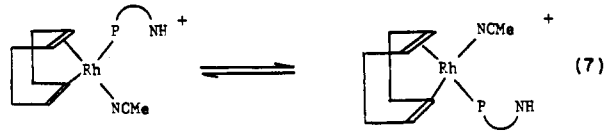
Scheme I. Pathway for the Exchange of Alkene Groups in Acetonitrile Solutions of Rh(1,5-COD)(MeCN)(PNH(CPhO))$^+$ (5)



(L = MeCN)

resonance also disappears and is replaced by a related resonance at δ 8.4. The phenyl and methylene resonances remain unchanged. At −50 °C, the ^{1}H NMR spectrum of **5** in CD_2Cl_2/CH_3CN shows no resonance at δ 4.5, but two new peaks are present. These two resonances appear at δ 5.2 and 3.8, and these resonances can be assigned to the olefinic protons of a 1,5-COD ligand; one of the peaks corresponds to an olefinic bond trans to a P-donor ligand and the other to an olefinic group trans to a N-donor. These observations can be interpreted on the basis of the exchange process shown in eq 6. Acetonitrile substitutes the coordinated iminol group, converting it into a free amide functionality. This conclusion is supported by the infrared solution spectrum of **5** in CH_3CN, which shows bands at 3410 (ν(NH)), 1685 (amide I), and 1510 cm^{-1} (amide II). Acetonitrile substitution occurs rather than perchlorate ion ligation. This is confirmed by the observed conductivity (Λ_M) of 165 Ω^{-1} cm^2 mol^{-1} (typical of a 1:1 electrolyte) for **5** in CH_3CN and also by the finding that the addition of excess n-$Bu_4N^+ClO_4^-$ to the solution causes no changes in the ^{1}H NMR spectrum. Finally the ^{31}P NMR spectrum of **5** in CD_2Cl_2/CH_3CN shows a single double resonance at δ 22.9 (^1J(RhP) = 148 Hz). This spectrum shows little change from that obtained in pure CD_2Cl_2, verifying that acetonitrile does not replace the phosphine ligand.

These NMR spectral changes can be explained on the basis of the cis–trans isomerization shown in eq 7. If the exchange

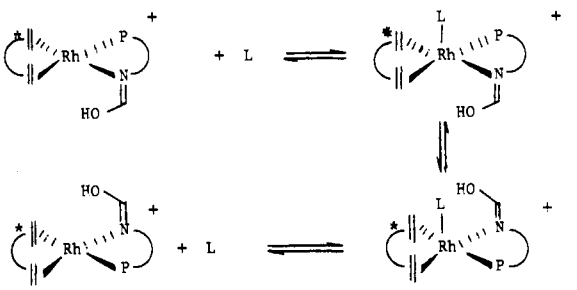


(7)

process simply involved acetonitrile substitution, then only the olefinic resonances of the 1,5-COD trans to phosphorus would be significantly shifted. The observed coalescence of the separate groups of olefinic resonances into a single line in the high-temperature (27 °C) limit confirms that the exchange process involves alkene interchange. We propose that the exchange process involves a 5-coordinate adduct with two acetonitrile molecules complexed to rhodium. This premise is supported by the observation that the olefinic proton resonance at δ 4.5 (27 °C) is narrowed by the addition of increased amounts of acetonitrile. This result supports an argument where CH_3CN, rather than the dangling amide arm of the hybrid ligand, coordinates in the fifth ligand position. In agreement the NH resonance of **5** is unaffected in position and width by changing either the temperature or the acetonitrile concentration. The pathway is outlined in Scheme I.

Analogous spectral changes are found in complex **6**, except that now the iminol ligand is not substituted by acetonitrile. In CD_2Cl_2 complex **6** shows olefinic resonances in the ^{1}H NMR spectrum at δ 5.3 and 3.4. Addition of acetonitrile causes these resonances to coalesce to a single broad peak at δ 4.3. The CH_2, OH, and phenyl resonances (Table I) remain unchanged. Lowering the temperature causes the coalesced resonance at δ 4.3 to separate into the individual olefinic resonances. The IR spectrum of **6** in acetonitrile solvent confirms that the iminol ligand is not replaced; bands at 1610, 1550, and 3320 cm^{-1} are observed due to ν(C=N), ν(C—O), and ν(OH) respectively. The conductivity value (Λ_M)

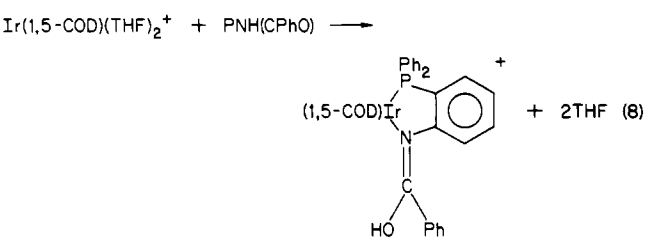
Scheme II. Pathway for the Exchange of Alkene Groups in Acetonitrile Solutions of Rh(1,5-COD)(P(CO)NHPh)$^+$ (6)



(L = MeCN)

of 161 Ω^{-1} cm^2 mol^{-1} in acetonitrile solution (0.96 mM) corresponds to a 1:1 electrolyte. The exchange pathway in **6** involving a single complexed acetonitrile molecule is shown in Scheme II. We have no explanation for the difference in the exchange pathways between **5** and **6** that we can confidently offer. Indeed the presence of a 5-membered ring in complex **5** could reasonably lead to the opposite prediction.

Compounds **7** and **8** are less well characterized. They are 1:1 electrolytes in both acetonitrile (for **7** Λ_M = 175 Ω^{-1} cm^2 mol^{-1} (0.72 mM); for **8** Λ_M = 176 Ω^{-1} cm^2 mol^{-1} (0.70 mM)) and dichloromethane solvent (for **7** Λ_M = 23.7 Ω^{-1} cm^2 mol^{-1} (0.72 mM); for **8** Λ_M = 14.9 Ω^{-1} cm^2 mol^{-1} (0.67 mM)). The complexes show the expected NMR resonances and IR bands due to the complexed iminol (Tables I and II). From these data it is apparent that the cationic iridium complexes are low-valent d^8 compounds that have not undergone N–H or O–H oxidative addition to give iridium(III) hydride complexes; the reaction of [Ir(1,5-COD)(THF)$_2$]ClO_4 with the hybrid ligands are simple substitutions to give the iminol chelates (eq 8 and 9).



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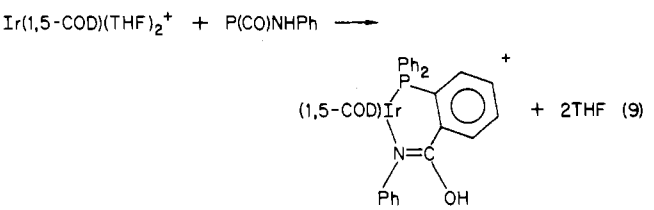
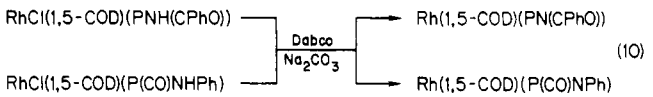


(9)

The complexes **1**–**4**, which have an uncoordinated amide ligand, can be deprotonated with base to give amido chelate complexes. Treating **1** and **2** as solutions in deoxygenated acetonitrile with Dabco and Na_2CO_3 gives Rh(1,5-COD)(PN(CPhO)) (**9**) and Rh(1,5-COD)(P(CO)NPh) (**10**) respectively (eq 10). In the



(10)

absence of sodium carbonate the reactions fail to go to completion. If triethylamine is used in place of Dabco, no reaction occurs. Complexes **9** and **10** are oxygen-sensitive yellow powders, which are soluble in CH_2Cl_2, $(CH_3)_2CO$, and CH_3CN. Solutions in acetonitrile are nonelectrolytes. The ^{31}P NMR ring shifts on chelation Δ_R are 22.0 ppm for **9** as compared to **1**, and 3.2 ppm for **10** as compared to **2**. This ring shift for **10** is unexpected since Δ_R values for 6-membered rings are usually to high field.[11] The

(11) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229–266.

infrared spectra of **9** and **10** show the absence of ν(NH) and the amide II bands. The amide I and III bands show the expected low-frequency shifts for the former, and the opposite shifts for the latter (for **9** (amide I, III) 1600, 1310 cm^{-1}; for **10** (amide I, III) 1600, 1360 cm^{-1}).

The reaction between IrCl(1,5-COD)(P(CO)NHPh) (**4**) and Dabco in a nitrogen-saturated dichloromethane solution gives Ir(1,5-CO)(P(CO)NPh) (**11**). Sodium carbonate is not required to effect complete reaction. The spectral properties are normal. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 8.8 singlet (Δ_R = 5.6 ppm). The compound IrCl(1,5-COD)(PNH(CPhO)) (**3**) reacts with Dabco to give an iridium(III) hydride complex. This compound and reaction will be discussed at the end of the next section.

Iridium(III) Hydride Complexes. Conceptually we have now arrived at a stage where oxidative addition of the N–H bond to Rh(I) and Ir(I) can be expected to occur. We have synthesized electron-rich coordinately unsaturated iridium(I) complexes with the protonated amido arm of the ligand complexed to the metal center, and it is realistic to assume that oxidative addition will be favorable. Indeed with the analogous iridium(I) compound complexed to a phosphino aldehyde ligand, C–H addition to give an iridium(III) complex has been found to occur.[1]

Two possible reasons for our nonobservance of N–H addition are realistic. The first possibility is that complexation of the amido ligand occurs via the iminol tautomer and that this isomer form does not lead to hydride formation. A second possibility is that the chelating 1,5-COD ligand is a sufficiently good π-acceptor to preferentially stabilize the iridium complex in its univalent d^8 state. This latter possibility is readily tested by replacing the 1,5-COD ligand on Ir(I) with phosphine donor ligands, which will impart a significantly larger electron density to the metal center. We have therefore replaced the 1,5-COD ligand with such stronger electron donors.

The complex $IrCl(PPh_3)_2$ is a 14-electron iridium(I) complex, which readily undergoes oxidative addition. The complex can be prepared in situ from the cyclooctene complex $[IrCl(C_8H_{14})_2]_2$ and 4 mol of triphenylphosphine (eq 11). Addition of 1 equiv

$$[IrCl(C_8H_{14})_2]_2 + 4PPh_3 \rightarrow 2IrCl(PPh_3)_2 + 4C_8H_{14} \qquad (11)$$

of PNH(CPhO) in oxygen-free dry toluene to a toluene solution of $IrCl(PPh_3)_2$ at 25 °C under nitrogen gives the iridium(III) hydride complex IrHCl(PN(CPhO))$(PPh_3)_2$ (**12**). Solutions of **12** are rapidly decomposed by oxygen, but the yellow complex can be handled in air for brief periods of time without noticeable deterioration. The complex is soluble in polar organic solvents.

The complex consists of two isomers which cannot be separated by chromatography on silica gel or Florisil. Solutions of **12** are nonelectrolytes in acetonitrile. The solid-state (Nujol) infrared spectrum of **12** (isomer A + B) shows the presence of a hydride and a deprotonated amido ligand. The N-deprotonated amido ligand is confirmed by the absence of ν(NH) and amide II bands, and also by the shifts in the amide I and III bands to 1595 and 1360 cm^{-1}. The presence of two isomeric hydrides is indicated by two absorption bands characteristic of ν(IrH) at 2200 and 2040 cm^{-1}. The band at 2200 cm^{-1} is characteristic of a hydride ligand on iridium(III) trans to a ligand low in the trans-influence series, and the low-frequency band at 2040 cm^{-1} is characteristic of an iridium(III) hydride with the ligand trans to a complexed phosphorus.[12]

The stereochemistry of the major isomer **12a** can be deduced by a combination of ^1H and ^{31}P NMR spectroscopy. The ^1H NMR spectrum in C_6D_6 is a doublet of doublets of a doublet at δ = −17.9 (^2J(PH) = 19, 10, 9 Hz). This spectrum requires a structure with these nonequivalent phosphorus ligands cis to the hydride. The $^{31}P\{^1H\}$ NMR spectrum of **12** is consistent with an ABC spin system. Such a spectrum lacks symmetry, and in a solution containing a mixture of two isomers, it is difficult to specifically identify which particular lines belong to which particular compound. Identification of the lines due to the major isomer **12a** from those of **12b** has been accomplished by repeating the synthesis several times and comparing peak intensities. Since the relative isomer yield varies slightly between preparations, we can assign which resonances are due separately to **12a** and **12b**. Analysis of the $^{31}P\{^1H\}$ NMR spectrum of **12a** gives $\delta(P_A)$ = 6.0, $\delta(P_B)$ = −6.0, $\delta(P_C)$ = −7.9, $^2J(P_AP_B)$ = 346 Hz, $^2J(P_AP_C)$ = 19 Hz, and $^2J(P_BP_C)$ = 18 Hz. The resonance $\delta(P_A)$ is downfield ring shifted and can be assigned to PN(CPhO). The upfield resonances $\delta(P_A)$ and $\delta(P_B)$ are characteristic of monodentate phosphines coordinated to iridium(III). The ^2J values show that PN(CPhO) is trans to one PPh_3 and cis to the other. The triphenylphosphine ligands are mutually cis. These data only leave one ambiguity resolved; stereochemistries A and B (Figure 3) are both compatible with the data.

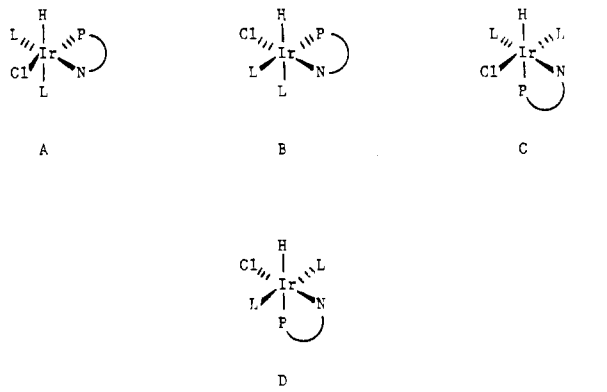
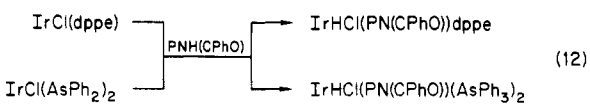


Figure 4. Possible stereochemistry of complex **12b** (L = PPh_3).

The stereochemistry of **12b** is less certain. The ^1H NMR spectrum shows a doublet of triplets with δ = −17.2 and ^2J(PH) = 364 and 16 Hz. This splitting pattern with a triplet and a large ^2J(PH) value is diagnostic of a stereochemistry with one phosphorus trans to hydride and two stereochemically equivalent phosphorus atoms cis to the hydride. Because of the low yield of **12b**, along with the complexity of the ^{31}P NMR spectrum of **12a,b**, we cannot unambiguously assign the peaks due to **12b** and be certain that we have collected all the peaks necessary to analyze the system as an A_2B pattern. From the ^1H NMR spectrum of **12b** we can only assign the stereochemistry as one of the four options A–D (Figure 4). In principle, structures A and B do not strictly meet the criterion of two equivalent cis phosphine ligands, however we cannot just assume that a cis-PH coupling constant between PN(CPhO) and PPh_3 will be significantly different to eliminate structures A and B. Nevertheless C or D is the preferred stereochemistry.

This chelate-assisted N–H addition to electron-rich iridium(I) complexes is not limited to the triphenylphosphine analogue. We have prepared IrCl(dppe) and $IrCl(AsPh_3)_2$ by an analogous procedure and have used these precursors to prepare IrHCl(PN(CPhO))dppe (**13**) and IrHCl(PN(CPhO))$(AsPh_3)_2$ (**14**) by N–H addition from PNH(CPhO) (eq 12). In each case iridium hydrides are formed as an isomeric mixture. Both **13** and **14** are yellow air-sensitive complexes, which are nonelectrolytes in acetonitrile solvent. For the synthesis of complex **13**, the reaction yields a major (**13a**) and a minor (**13b**) isomer. For **13a** the isomer possibilities are A and B, and for **13b** they are C, D and E (Figure 5). Structure C is probably the correct one for complex **13b** because the two cis phosphorus ligands are both dppe phosphorus ligating atoms and are therefore more correctly assigned as equivalent phosphorus atoms.



(12)

For the triphenylarsine analogue **14** we find two isomers **14a** and **14b**, which are in an approximate 2:1 ratio. No isomer is found where the hydride is trans to phosphorus. By analogy with complexes **12** and **13**, we believe that **14a** has the hydride trans to N or Cl, and that **14b** has hydride trans to As.

(12) Jesson, J. P. In "Transition Metal Hydrides"; Muetterties, E. L., Ed.; Dekker: New York, 1971; Chapter 4.

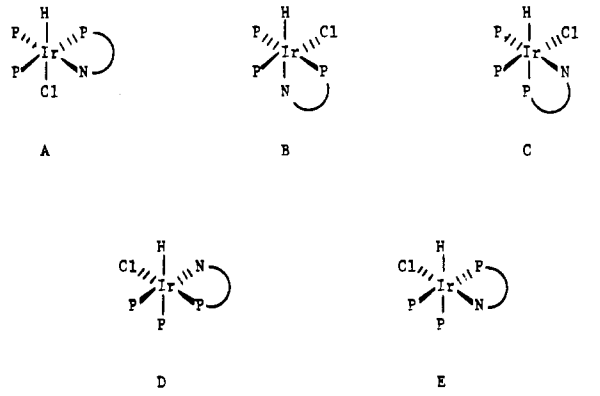


Figure 5. Isomer possibilities for complexes **13a,b**.

It is apparent from these complexes **12**, **13**, and **14** that N-H addition to iridium(I) will occur with the ligand PNH(CPhO). Although the reaction is apparently induced by intramolecular cyclization, this premise needs to be tested. We have therefore mixed $IrCl(PPh_3)_2$ with 1 mol of benzamide or benzanilide, both with and without 1 equiv of added triphenylphosphine. These conditions are designed to mimic those used to prepare complex **12**. The first experiment with no added PPh_3 is designed to simulate a pathway for PNH(CPhO) addition where N-H cleavage by $IrCl(PPh_3)_2$ is the initial step. The second experimental condition with 1 mol of added PPh_3 reproduces the conditions for a pathway where phosphine complexation is the first step, and N-H addition is induced by $IrCl(PPh_3)_3$. The only difference between PNH(CPhO) and these above sets of conditions is the intramolecularity of NH additions from PNH(CPhO). Under the two sets of conditions with added benzamide or benzanilide we observe, by IR spectroscopy, no loss of the amide N-H functionality or the formation of an iridium hydride. Our claim of intramolecular "chelate-assisted" oxidative addition with PNH(CPhO) therefore appears to be justified.

Now that our finding of iridium(III) hydrides from PNH(CPhO) and iridium(I) complexes is fully justified, we must return to discuss the formation of the hydride complex IrHCl(1,5-COD)(PN(CPhO)) (**15**) from the treatment of IrCl(1,5-COD)(PNH(CPhO)) with Dabco. The reaction was carried out with the amido iridium(I) complex Ir(1,5-COD)(PN(CPhO)) being the targeted product. Complex **15** shows no IR bands due to ν(NH) or amide II, but shifted amide I and III bands at 1610 and 1330 cm^{-1} are observed. Medium-intensity bands due to ν(IrH) are found at 2160 and 2140 cm^{-1}. We do not find a hydride resonance in the ^1H NMR spectrum (CD_2Cl_2 solvent). The phenyl, methylene, and olefinic protons are in the expected regions (Table I). The $^{31}P\{^1H\}$ NMR spectrum (CD_2Cl_2 solvent) shows a broad resonance at δ 15.4 ($\nu_{1/2}$ = 12 Hz) at 27 °C, which shifts and narrows to δ 9.4 ($\nu_{1/2}$ = 3 Hz) at -72 °C. It appears therefore that the complex is undergoing intramolecular exchange, which may explain why the upfield hydride resonance is not observed.[13]

It is not obvious at present as to why this hydride complex, **15**, is formed under the identical experimental conditions that can be used to prepare compounds **9**, **10**, and **11**. A plausible explanation is that an initially formed anionic iridium(I) complex $IrCl(1,5\text{-}COD)(PN(CPhO))^-$ is protonated at iridium by $DabcoH^+$ faster than it undergoes chloride ion loss, resulting in the formation of IrHCl(1,5-COD)(PN(CPhO)). Nevertheless this explanation remains speculative, and further investigation of these amido complexes of the later transition metals is needed before variations in their reaction chemistry can be fully explained.

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Solid-State Structure of α-$Mo_2Cl_4(dppe)_2$ and Its Transformation to β-$Mo_2Cl_4(dppe)_2$. Evidence for the Internal Flip Mechanism

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The crystal structure of α-$Mo_2Cl_4(dppe)_2 \cdot OC_4H_8$, in which the two dppe ligands chelate each of the Mo atoms of the dimer, has been determined. The space group is $C2/c$ with a = 32.946 (5) Å, b = 9.876 (4) Å, c = 23.179 (3) Å, β = 119.67 (1)°, V = 6548 (7) Å^3, and Z = 4. The midpoint of the Mo-Mo unit resides on an inversion center. The Mo-Mo bond distance is 2.140 (2) Å, and the mean Mo-P and Mo-Cl distances are 2.548 [2] Å and 2.423 [1] Å, respectively. The light brown product of the solid-state transformation of α-$Mo_2Cl_4(dppe)_2$ was characterized by its far-IR spectrum, which is identical with that of pure crystalline β-$Mo_2Cl_4(dppe)_2$. The same transformation in CH_2Cl_2 solution was found to be a reversible process of the first order in both directions. The initial rate constant, assumed to be that of the forward process, was 1.13×10^{-5} s^{-1}, and the rate constant for approach to equilibrium, which is a sum of the rate constants for the forward and reverse processes, was found to be 1.22×10^{-5} s^{-1}. These rates were essentially unaffected by the presence of a 20-fold excess of dppe. These results provide support for our earlier proposal that the isomerization processes occur by an "internal flip" of the Mo_2 unit within the ligand cage.

Introduction

The synthesis of single crystals of both α- and β-$Mo_2Cl_4(dppe)_2$, which were originally prepared by Walton and co-workers,[1] and the crystal structure of β-$Mo_2Cl_4(dppe)$ have been described in a previous publication by the present authors.[2] The isomerization of the α-isomer to the β-isomer in CH_2Cl_2 solution was known to occur[3] and has been studied in detail.[4] A mechanism involving an internal reorientation (or internal flip) of the Mo_2^{4+} moiety inside the cavity formed by the eight ligand atoms was proposed[5] for a similar reaction of α-$Mo_2Br_4(dppe)_2$ on the basis of the observed first-order nature of the process and other considerations.

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