Contribution No. 5255 from the Arthur Amos Noyes Laboratory of Chemical Physics,
California Institute of Technology, Pasadena, California 91125,
and the Departments of Chemistry, Clarkson College of Technology, Potsdam, New York 13676,
and The Pennsylvania State University, University Park, Pennsylvania 16802

Electronic Spectral Studies of Planar Rhodium(I) and Iridium(I) Complexes Containing π-Acceptor Ligands

ROSEMARY BRADY, BRENDAN R. FLYNN, GREGORY L. GEOFFROY,*[1a] HARRY B. GRAY,*[1b] J. PEONE, Jr., and L. VASKA*[1c]

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Electronic absorption spectra have been measured in benzene and some related solutions at 25 °C for the following series of planar d^8 complexes of the general formula *trans*-[M(A)(CO)L_2]: (1) M = Rh, L = $(C_6H_5)_3P$; A = $OClO_3$, $OReO_3$, OCO_2H, OH, $O_2P(OH)_2$, F, ONO_2, N_3, SH, Cl, Br, NCO, NO_2, $N(CN)_2$, I, NCS, $NCBH_3$, SCO_2H, CN; (2) (a) M = Rh, A = Cl; L = $(C_6F_5)_3P$, $(C_6H_5)_3As$, $(C_2H_5)_3P$, $(C_6H_5)_3Sb$, $(p\text{-}CH_3OC_6H_4)_3P$, $(m\text{-}CH_3C_6H_4)_3P$; (2) (b) M = Rh, A = I; L = $(C_6H_{11})_3P$, $(m\text{-}CH_3C_6H_4)_3P$, $(C_6H_5)_3P$; (3) M = Ir, L = $(C_6H_5)_3P$; A = OH, F, OCO_2H, ONO_2, Cl, $OReO_3$, $OClO_3$, N_3, NCO, Br, NCS, NO_2, I, NCSe, CN; (4) M = Ir, A = Cl; L = $(o\text{-}CH_3C_6H_4)_3P$, $(C_6H_{11})_3P$, $(C_6H_5)_2(C_2H_5)P$, $(C_6H_5)_2(C_4H_9)P$, $(C_6H_5)_3As$, $(p\text{-}CH_3OC_6H_4)_3P$, $(p\text{-}ClC_6H_4)_3P$, $(p\text{-}CH_3C_6H_4)_3P$, $(m\text{-}CH_3C_6H_4)_3P$; (5) M = Ir, A = $NCBH_3$, L = $(C_6H_{11})_3P$. The orders of the derivatives listed in the individual series correspond to decreasing energies of the longest wavelength absorption bands in the visible spectra. The principal low-energy bands in the complexes are assigned as metal-to-ligand charge-transfer transitions of the type $d_{z^2} \rightarrow b_1\pi$.

Introduction

The activation of small molecules (XY) by metal complexes (ML_i) through oxidative addition reactions has been extensively investigated in recent years. Although most studies have been concerned with the preparation of new compounds and their characterization, a few have also dealt with the rates and equilibria of the reactions.

Chlorocarbonylbis(triphenylphosphine)iridium(I)[2] and a series of related isoelectronic and isostructural complexes *trans*-[M(A)(CO)L_2] (M = Ir(I), Rh(I); A = anionic ligand; L = monodentate tertiary phosphine or arsine), in particular, have been examined in detail.[3] The presence of the CO ligand in *trans*-[IrCl(CO)$(Ph_3P)_2$] provided a singular means of detecting reactions, following their course, and inquiring into the nature of the products, [(XY)IrCl(CO)$(Ph_3P)_2$], through the extent of the accompanying ν_{CO} shifts.[4] These observations were later analyzed in semiquantitative terms, and the $\Delta\nu_{CO}$'s were found to provide useful information for a general assessment of the reactions of these types of compounds.[3] However, as the number of different derivatives of *trans*-[M(A)(CO)L_2] grew, it became apparent that this spectral label is not always subject to a straightforward interpretation.[5] Furthermore, new planar complexes of Ir(I), Rh(I), and Co(I) not containing CO were synthesized and found to undergo oxidative addition reactions.[6] Accordingly, a need arose for a more fundamental study of the electronic structures of these d^8 complexes.

The complex *trans*-[IrCl(CO)$(Ph_3P)_2$] exhibits three well-defined absorption bands in the visible spectral region. As these bands virtually disappear on addition of H_2, HCl, and O_2 to form six-coordinate complexes of iridium(III), [(XY)IrCl(CO)$(Ph_3P)_2$], they were used to follow the kinetics of oxygenation and hydrogenation of *trans*-[IrCl(CO)$(Ph_3P)_2$].[7] Analogous spectral changes subsequently became a standard method for investigating the kinetic behavior of a multitude of reactions of Ir(I), Rh(I), and Co(I) species with numerous molecules (XY).[6b,c,8] In the course of inquiring into the reactivity and stability patterns of these low-spin d^8 complexes, a correlation was discovered between the activation enthalpies of the addition reactions and the visible spectra of the starting compounds, ML_i. For example, in a series of Co(I), Rh(I), and Ir(I) complexes, the activation enthalpy of oxygenation was found to be proportional to the energy of the lowest electronic transition.[6b] However, during all of these studies, as well as numerous kinetic investigations elsewhere,[9] little if any attention was paid to the assignment of the ML_i spectral bands, except that they were sometimes tacitly assumed to be due to d–d transitions.[6b,c,8b,c]

Planar iridium(I) and rhodium(I) complexes containing bidentate phosphine ligands, $[M(PC_2P)_2]^+$ and $[M(PC{=}CP)_2]^+$,[10] display electronic absorption spectra remarkably similar to the *trans*-[M(A)(CO)L_2] compounds.[6b,11] For example, $[Ir(PC_2P)_2]^+$ exhibits three absorption bands in the visible spectral region with extinction coefficients comparable to those of the corresponding three bands of *trans*-[IrCl(CO)$(Ph_3P)_2$]. The large molar extinction coefficients of the absorption bands, the lack of any intensity decrease upon cooling, the energy ordering Ir(I) < Rh(I) < Pt(II), and the MCD spectra of $[M(PC_2P)_2]^+$ and $[M(PC{=}CP)_2]^+$ have established that the responsible transitions are of the metal-to-ligand charge-transfer (MLCT) type.[11] The two low-lying bands in each complex have been assigned to the $d_{z^2} \rightarrow a_{2u}\pi$ transitions $^1A_{1g} \rightarrow E_u(^3A_{2u})$ and $^1A_{1g} \rightarrow A_{2u}(^1A_{2u})$, respectively. In this article we present an analogous interpretation for the electronic spectra of *trans*-[M(A)(CO)L_2] complexes.

Experimental Section

The compounds were prepared as described elsewhere.[2,5,8b,c,12,13]

The electronic absorption spectra of ca. 10^{-4} M solutions at 298 K were measured with Zeiss PMQ-II, Bausch and Lomb Precision, and/or Cary 14 spectrophotometers by using 1.00- or 2.00-cm thermostated quartz, Suprasil, and/or Pyrex cells. The data for iridium complexes (sensitive to oxygen) were obtained from degassed solutions and in some instances also under prepurified nitrogen (no difference in the results was found). The solutions of the rhodium complexes (relatively insensitive to oxygen) were measured in air or in the degassed state. Spectral grade commercial solvents were used.

At liquid nitrogen temperature, the spectra were obtained using a Dewar flask fitted with Suprasil quartz windows and modified to hold a standard 1.00-cm cell. Measurements were performed in a 5:5:2 ethyl ether–isopentane–ethyl alcohol (EPA) solution and the low-temperature spectra were corrected for solvent contraction. It was necessary to dissolve the complexes in 1–2 drops of $CHCl_3$ before addition of EPA.

Results

Electronic absorption spectral data for the *trans*-[M(A)(CO)L_2] complexes are summarized in Table I. The spectra of [RhCl(CO)$(Ph_3P)_2$] and [IrCl(CO)$(Ph_3P)_2$] at 298 and 77 K are shown in Figures 1 and 2, respectively. For a few of the iridium complexes listed in Table I and for others with

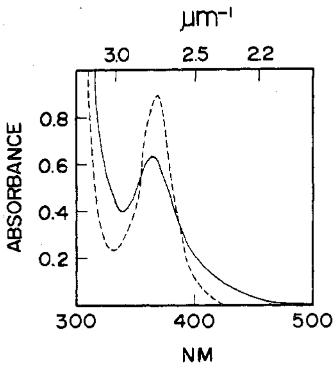

Figure 1. Electronic absorption spectra of $[RhCl(CO)(Ph_3P)_2]$ in EPA solution at 298 (——) and 77 K (- - - -).

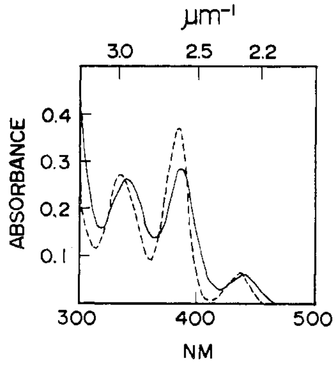

Figure 2. Electronic absorption spectra of $[IrCl(CO)(Ph_3P)_2]$ in EPA solution at 298 (——) and 77 K (- - - -).

different tertiary phosphines (L) spectral data obtained from toluene or cyclohexane solutions at 293 K have been reported previously.[14] These results are in general agreement with our measurements.

At room temperature the spectrum of each of the rhodium complexes shows a single, relatively broad band in the visible–near-uv region (Table I). The position of this band varies in energy from 2.49 to 2.89 μm^{-1} and in extinction coefficient from ca. 2500 to 5000 $M^{-1}\ cm^{-1}$. In frozen solutions at 77 K, the 2.73-μm^{-1} band in the spectrum of $[RhCl(CO)(Ph_3P)_2]$ exhibits a pronounced sharpening, but there is no loss of integrated intensity (Figure 1). Similar temperature effects have been observed for the low-lying absorption bands of $[Rh(PC_2P)_2]^+$ and $[Rh(PC{=}CP)_2]^+$,[11] which exhibit no loss of intensity upon cooling. Spectral measurements on these complexes have also revealed the presence of a second absorption band at lower energy. This second feature was not resolved in the 77-K spectrum of $[RhCl(CO)(Ph_3P)_2]$.

Each of the $[Ir(A)(CO)L_2]$ complexes shows three bands in the visible spectral region (Table I). The band at lowest energy is always less intense (ϵ ~400–1000) than the remaining two (ϵ ~2000–5000) and varies in energy from 2.04 to 2.39 μm^{-1}. Upon cooling an EPA solution of $[IrCl(CO)(Ph_3P)_2]$ to 77 K, these spectral bands sharpen and shift slightly in position but do not lose integrated intensity (Figure 2).

The order of the derivatives listed in Table I corresponds to decreasing energies of the longest wavelength spectral bands. The spectrochemical orders for the ligands A and L are as follows. **Anionic ligands (A)**: $[Rh(A)(CO)(Ph_3P)_2]$: $OClO_3 > OReO_3 > OCO_2H > OH > O_2P(OH)_2$, $F > ONO_2 > N_3 > SH > Cl > Br$, $NCO > NO_2$, $N(CN)_2 > I > NCS > NCBH_3 > SCO_2H > CN$. $[Ir(A)(CO)(Ph_3P)_2]$: $OH > F > OCO_2H > ONO_2 > Cl$, $OReO_3 > OClO_3 > N_3$, NCO, $Br > NCS$, NO_2, $I > NCSe > CN$. **Neutral ligands (L)**: $[RhCl(CO)L_2]$: $(C_6F_5)_3P > (C_6H_5)_3As > (C_2H_5)_3P > (C_6H_5)_3Sb > (p\text{-}CH_3OC_6H_4)_3P$, $(m\text{-}CH_3C_6H_4)_3P > (C_6H_5)_3P$. $[IrCl(CO)L_2]$: $(o\text{-}CH_3C_6H_4)_3P > (C_6H_{11})_3P > (C_6H_5)_2(C_2H_5)P$, $(C_6H_5)_2(C_4H_9)P > (C_6H_5)_3As > (p\text{-}CH_3OC_6H_4)_3P > (p\text{-}ClC_6H_4)_3P$, $(C_6H_5)_3P > (p\text{-}CH_3C_6H_4)_3P$, $(m\text{-}CH_3C_6H_4)_3P$.

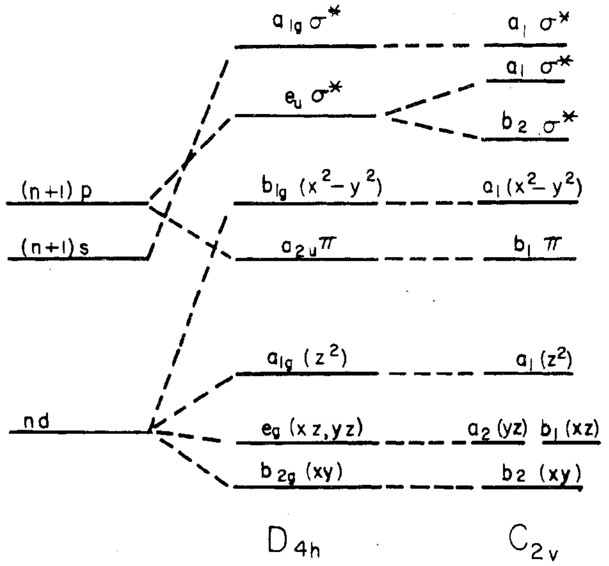

Figure 3. Molecular orbital energy level correlation diagram for planar D_{4h} and C_{2v} complexes. In the C_{2v} case, x is taken as the C_2 axis and z is perpendicular to the molecular plane.

In general, the absorption bands in the spectra of the iridium(I) complexes are somewhat sharper than those of the rhodium(I) derivatives. Thus, the spectrochemical orders for the ligands are somewhat better defined for the Ir(I) compounds.

Discussion

The large and temperature-independent intensities of the absorption bands in the C_{2v} complexes $[RhCl(CO)(Ph_3P)_2]$ and $[IrCl(CO)(Ph_3P)_2]$ establish that the responsible electronic transitions are fully allowed. It is reasonable to propose that the low-lying bands in the *trans*-$[M(A)(CO)L_2]$ complexes are attributable to transitions analogous to $d \rightarrow a_{2u}\pi$ in D_{4h} symmetry, in view of close similarities to the spectra of the $[M(PC_2P)_2]^+$ and $[M(PC{=}CP)_2]^+$ ions. The energy ordering Ir(I) < Rh(I) in the C_{2v} complexes is fully consistent with such MLCT assignments. Interpretation of the lowest MLCT bands may be made by reference to the molecular orbital level diagram shown in Figure 3. The lowest band in the rhodium complexes is assigned to the $d_{z^2} \rightarrow b_1\pi$ transition $^1A_1 \rightarrow B_1(^1B_1)$, and the two low-lying bands in the iridium complexes are assigned, respectively, to $^1A_1 \rightarrow A_1$, $B_2(^3B_1)$, and $^1A_1 \rightarrow B_1$. Both experimental[15] and theoretical[16] studies on $[Pt(CN)_4]^{2-}$, $[Ir(CNC_2H_5)_4]^+$, and $[Pt(CNC_2H_5)_4]^{2+}$ have shown that the A_{2u} excited state is a spin–orbit hybrid of ^3E_u and $^1A_{2u}$, and it is probable that B_1 is similarly spin–orbit mixed in the *trans*-$[Ir(A)(CO)L_2]$ complexes.[17]

We are now able to comment on the position of the absorption bands in the $[M(A)(CO)L_2]$ complexes as the ligand A is varied. Clearly, the energy ordering $Br > NO_2$, $I > CN$ is inconsistent with assignment of the bands as ligand field transitions, as the usual spectrochemical series is $CN > NO_2 \gg Br > I$. The observed ordering, however, is consistent with an MLCT interpretation and may be rationalized in terms of the influence of the ligands on the relative positioning of the d_{z^2} and $b_1\pi$ levels (Figure 3). Strong π-accepting ligands should greatly stabilize the $b_1\pi$ level, whereas strong σ-donor ligands should destabilize d_{z^2}. Many π-accepting ligands are also good σ donors (e.g., CN) and thus should be found low

Table I. Electronic Absorption Spectral Data for *trans*-$[M(A)(CO)L_2]$ at 298 K[a]

Complex	λ_{max}, nm	E_{max}, μm^{-1}	ϵ_{max}, M^{-1} cm^{-1}	Medium
$[Rh(A)(CO)((C_6H_5)_3P)_2]$				
A = $OClO_3$	350	2.86	3160	C_6H_6
$OReO_3$	352	2.84	3410	C_2H_5OH
OCO_2H	355	2.82	3040	C_2H_5OH
	366^b	2.73^b		Nujol
OH	356	2.81	2560	C_2H_5OH
	370^b	2.70^b		Nujol
$O_2P(OH)_2$	358^b	2.79^b		C_6H_6
F	358	2.79	4000	C_6H_6
ONO_2	363	2.75	3480	C_6H_6
N_3	365	2.74	4220	C_6H_6
SH	366	2.73	4880	C_6H_6
Cl	367	2.72	3780	C_6H_6
	367	2.72	5370	EPA, 77 K
Br	369	2.71	3680	C_6H_6
NCO	369	2.71	4320	C_6H_6
NO_2	370	2.70	2960	C_6H_6
$N(CN)_2$	370	2.70	4160	C_6H_6
I	372	2.69	3720	C_6H_6
NCS	373	2.68	4270	C_6H_6
$NCBH_3$	374	2.67	4220	C_6H_6
SCO_2H	384	2.60	2790	C_2H_5OH
CN	402	2.49	4270	C_6H_6
$[RhCl(CO)L_2]$				
L = $(C_6F_5)_3P$	346	2.89	3220	C_6H_6
$(C_6H_5)_3As$	356	2.81	4240	C_6H_5Cl
$(C_2H_5)_3P$	364	2.75	3220	C_6H_5Cl
$(C_6H_5)_3Sb$	365	2.74	3700	C_6H_5Cl
$(p\text{-}CH_3OC_6H_4)_3P$	366	2.73		C_6H_6
$(m\text{-}CH_3C_6H_4)_3P$	366	2.73	3880	C_6H_6
$(C_6H_5)_3P$	367	2.72	3780	C_6H_6
$[RhI(CO)L_2]$				
L = $(C_6H_{11})_3P$	369	2.71	2430	C_6H_6
$(m\text{-}CH_3C_6H_4)_3P$	370	2.70	3420	C_6H_6
$(C_6H_5)_3P$	372	2.69	3720	C_6H_6
$[Ir(A)(CO)((C_6H_5)_3P)_2]$				
A = OH	420	2.38	640	C_6H_6
	382	2.62	2480	
	353	2.83		
	430	2.32		Nujol[b]
	390	2.56		
F	427	2.34	820	C_6H_6
	378	2.64	4300	
	335	2.98	3740	
OCO_2H	434	2.30	510	C_2H_5OH
	382	2.62	1750	
	440	2.27		Nujol
	385	2.60		
	330	3.03		
ONO_2	437	2.29	540	C_6H_6
	386	2.59	2900	
	333	3.00	3100	
Cl	439	2.28	730	C_6H_6
	387	2.58	4040	
	339	2.95	3160	
	436	2.29	792	EPA, 77 K
	384	2.60	5209	
	335	2.98	3282	
	439	2.28		Nujol
	387	2.58		
	339	2.95		
$OReO_3$	439	2.27	970	C_6H_6
	391	2.56	3300	
	339	2.95	3930	
	440	2.27		Nujol
	390	2.56		
	340	2.96		
$OClO_3$	440	2.27	590	C_6H_6
	387	2.58	2650	
	327	3.06	3080	
	440	2.27		Nujol
	387	2.58		
	327	3.06		
$[Ir(A)(CO)((C_6H_5)_3P)_2]$				
A = N_3	442	2.26	740	C_6H_6
	392	2.55	3600	
	347	2.88	3200	
NCO	443	2.26	830	C_6H_6
	387	2.58	4810	
	340	2.94	3170	
Br	443	2.26	800	C_6H_6
	390	2.56	3960	
	343	2.92	3100	
NCS	450	2.22	1050	C_6H_6
	395	2.53	4670	
	350	2.86	3170	
NO_2	450	2.22	360	C_6H_6
	398	2.51	2200	
	328	3.05	2600	
I	451	2.22	590	C_6H_6
	397	2.52	2570	
	356	2.81	2100	
NCSe	452	2.21	930	C_6H_6
	397	2.52	3420	
	358	2.79	4050	
CN	490	2.04	470	C_6H_6
	423	2.36	3470	
	367	2.72	3620	
$[IrCl(CO)L_2]$				
L = $(o\text{-}CH_3C_6H_4)_3P$	418	2.39	580	C_6H_6
	376	2.66	2540	
	329	3.04	2790	
	419	2.39		Nujol
	372	2.69		
	324	3.09		
$(C_6H_{11})_3P$	430	2.32	680	C_6H_6
	379	2.64	3490	
	337	2.97	2430	
	432	2.31		Nujol
	379	2.64		
	336	2.98		
$(C_6H_5)_2(C_2H_5)P$	434	2.30	590	C_6H_6
	381	2.62	3390	
	335	2.98	2690	
$(C_6H_5)_2(C_4H_9)P$	434	2.30		C_6H_6
	382	2.62		
	334	2.92		
$(C_6H_5)_3As$	436	2.29	680	C_6H_5Cl
	387	2.58	2840	
	343	2.92	2890	
$(p\text{-}CH_3OC_6H_4)_3P$	437	2.29	430	C_6H_6
	383	2.61	4180	
	335	2.98	4200	
$(p\text{-}ClC_6H_4)_3P$	438	2.28	530	C_6H_6
	387	2.58	4300	
	338	2.96	3340	
$(C_6H_5)_3P$	439	2.28	730	C_6H_6
	387	2.58	4040	
	339	2.95	3160	
	434	2.28		Nujol
	387	2.58		
	339	2.95		
$(p\text{-}CH_3C_6H_4)_3P$	440	2.27	680	C_6H_6
	385	2.60	3670	
	339	2.95	2950	
	440	2.27		Nujol
	389	2.57		
	333	3.00		
$(m\text{-}CH_3C_6H_4)_3P$	440	2.27	740	C_6H_6
	386	2.59	4080	
	339	2.95	3120	
	440	2.27		Nujol
	390	2.56		
	335	2.98		
$[Ir(NCBH_3)(CO)((C_6H_{11})_3P)_2]$	452	2.21	530	C_6H_6
	425	2.35	480	
	396	2.52	3880	
	346	2.89	3740	

[a] λ_{max}, *ca.* ±1 nm; ϵ_{max}, ca. ±2%. [b] Broad band, ca. ±5 nm.

in the ordering of the least energetic $d_{z^2} \rightarrow b_1\pi$ transition. The position of CN at the least energetic end of the series for both the Rh(I) and Ir(I) complexes is consistent with this interpretation.

The energy ordering F > Cl > Br > I may also be rationalized in terms of an MLCT assignment, as the π-accepting strength of the halide ligand in these complexes is believed to vary according to I > Br > Cl > F. The latter ordering was derived from an analysis of the carbonyl stretching frequencies of *trans*-[M(A)(CO)L$_2$] complexes in which the total electronegativity of the ligand A was partitioned into σ and π components.[5] Also, the σ to metal electron donation may increase according to I > Br > Cl > F, giving a d_{z^2} ordering consistent with the experimental positioning of the least energetic $d_{z^2} \rightarrow b_1\pi$ transition.

The relative ordering of the $d_{z^2} \rightarrow b_1\pi$ transitions as L is varied in the *trans*-[MCl(CO)L$_2$] complexes is probably a complicated function of the σ-donor and π-acceptor properties of L. The spectral differences in most cases, however, are relatively small to make any meaningful correlations of band maxima with electronic structural features.

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Registry No. *trans*-[Rh(OClO$_3$)(CO)((C$_6$H$_5$)$_3$P)$_2$], 32354-26-0; *trans*-[Rh(OReO$_3$)(CO)((C$_6$H$_5$)$_3$P)$_2$], 59092-45-4; *trans*-[Rh(OCO$_2$H)(CO)((C$_6$H$_5$)$_3$P)$_2$], 59168-80-8; *trans*-[Rh(OH)(CO)((C$_6$H$_5$)$_3$P)$_2$], 32354-36-2; *trans*-[Rh(O$_2$P(OH)$_2$)(CO)((C$_6$H$_5$)$_3$P)$_2$], 59168-79-5; *trans*-[Rh(F)(CO)((C$_6$H$_5$)$_3$P)$_2$], 22481-17-0; *trans*-[Rh(ONO$_2$)(CO)((C$_6$H$_5$)$_3$P)$_2$], 22654-78-0; *trans*-[Rh(N$_3$)(CO)((C$_6$H$_5$)$_3$P)$_2$], 32354-30-6; *trans*-[Rh(SH)(CO)((C$_6$H$_5$)$_3$P)$_2$], 59122-90-6; *trans*-[Rh(Cl)(CO)((C$_6$H$_5$)$_3$P)$_2$], 15318-33-9; *trans*-[Rh(Br)(CO)((C$_6$H$_5$)$_3$P)$_2$], 17070-17-6; *trans*-[Rh(NCO)(CO)((C$_6$H$_5$)$_3$P)$_2$], 23028-37-7; *trans*-[Rh(NO$_2$)(CO)((C$_6$H$_5$)$_3$P)$_2$], 32354-24-8; *trans*-[Rh(N(CN)$_2$)(CO)((C$_6$H$_5$)$_3$P)$_2$], 32354-25-9; *trans*-[Rh(I)(CO)((C$_6$H$_5$)$_3$P)$_2$], 21006-49-5; *trans*-[Rh(NCS)(CO)((C$_6$H$_5$)$_3$P)$_2$], 17966-78-8; *trans*-[Rh(NCBH$_3$)(CO)((C$_6$H$_5$)$_3$P)$_2$], 36606-39-0; *trans*-[Rh(SCO$_2$H)(CO)((C$_6$H$_5$)$_3$P)$_2$], 59110-08-6; *trans*-[Rh(CN)(CO)((C$_6$H$_5$)$_3$P)$_2$], 32109-05-0; *trans*-[RhCl(CO)((C$_6$F$_5$)$_3$P)$_2$], 18956-21-3; *trans*-[RhCl(CO)((C$_6$H$_5$)$_3$As)$_2$], 16970-35-7; *trans*-[RhCl(CO)((C$_2$H$_5$)$_3$P)$_2$], 15631-52-4; *trans*-[RhCl(CO)((C$_6$H$_5$)$_3$Sb)$_2$], 33679-73-1; *trans*-[RhCl(CO)((*p*-CH$_3$OC$_6$H$_4$)$_3$P)$_2$], 16970-33-5; *trans*-[RhCl(CO)((*m*-CH$_3$C$_6$H$_4$)$_3$P)$_2$], 59122-91-7; *trans*-[RhI(CO)((C$_6$H$_{11}$)$_3$P)$_2$], 59092-46-5; *trans*-[RhI(CO)((*m*-CH$_3$-C$_6$H$_4$)$_3$P)$_2$], 59092-47-6; *trans*-[Ir(OH)(CO)((C$_6$H$_5$)$_3$P)$_2$], 32356-70-0; *trans*-[Ir(F)(CO)((C$_6$H$_5$)$_3$P)$_2$], 32356-62-0; *trans*-[Ir(OCO$_2$H)(CO)((C$_6$H$_5$)$_3$P)$_2$], 59168-78-4; *trans*-[Ir(ONO$_2$)(CO)((C$_6$H$_5$)$_3$P)$_2$], 32356-69-7; *trans*-[Ir(Cl)(CO)((C$_6$H$_5$)$_3$P)$_2$], 15318-31-7; *trans*-[Ir(OReO$_3$)(CO)((C$_6$H$_5$)$_3$P)$_2$], 59092-44-3; *trans*-[Ir(OClO$_3$)(CO)((C$_6$H$_5$)$_3$P)$_2$], 32356-67-5; *trans*-[Ir(N$_3$)(CO)((C$_6$H$_5$)$_3$P)$_2$], 21414-23-3; *trans*-[Ir(NCO)(CO)((C$_6$H$_5$)$_3$P)$_2$], 28195-62-2; *trans*-[Ir(Br)(CO)((C$_6$H$_5$)$_3$P)$_2$], 15842-08-7; *trans*-[Ir(NCS)(CO)((C$_6$H$_5$)$_3$P)$_2$], 28195-61-1; *trans*-[Ir(NO$_2$)(CO)((C$_6$H$_5$)$_3$P)$_2$], 31847-96-8; *trans*-[Ir(I)(CO)((C$_6$H$_5$)$_3$P)$_2$], 19472-16-3; *trans*-[Ir(NCSe)(CO)((C$_6$H$_5$)$_3$P)$_2$], 32356-64-2; *trans*-[Ir(CN)(CO)((C$_6$H$_5$)$_3$P)$_2$], 32109-04-9; *trans*-[IrCl(CO)((*o*-CH$_3$-C$_6$H$_4$)$_3$P)$_2$], 34054-05-2; *trans*-[IrCl(CO)((C$_6$H$_{11}$)$_3$P)$_2$], 34054-07-4; *trans*-[IrCl(CO)((C$_6$H$_5$)$_2$(C$_2$H$_5$)P)$_2$], 23723-99-1; *trans*-[IrCl(CO)((C$_6$H$_5$)$_2$(C$_4$H$_9$)P)$_2$], 28766-34-9; *trans*-[IrCl(CO)((C$_6$H$_5$)$_3$As)$_2$], 23954-42-9; *trans*-[IrCl(CO)((*p*-CH$_3$OC$_6$H$_4$)$_3$P)$_2$], 34054-03-0; *trans*-[IrCl(CO)((*p*-Cl-C$_6$H$_4$)$_3$P)$_2$], 34275-84-8; *trans*-[IrCl(CO)((*p*-CH$_3$C$_6$H$_4$)$_3$P)$_2$], 28195-56-4; *trans*-[IrCl(CO)((*m*-CH$_3$C$_6$H$_4$)$_3$P)$_2$], 34054-06-3; *trans*-[Ir(NCBH$_3$)(CO)((C$_6$H$_{11}$)$_3$P)$_2$], 36606-38-9.

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(10) PC$_2$P is 1,2-bis(diphenylphosphino)ethane; PC=CP is *cis*-1,2-bis(diphenylphosphino)ethylene; note that in earlier papers[6b,11] we have used different abbreviations, 2-phos (PC$_2$P) and 2=phos (PC=CP).

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