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Synthesis and Reactions of and Catalytic Homogeneous Hydrogenation by Chlorocarbonyl(*o*-(diphenylphosphino)-*N*,*N*-dimethylaniline)iridium(I) and Chlorocarbonyl(*o*-(diphenylphosphino)-*N*,*N*-dimethylbenzylamine)iridium(I)

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Complexes IrCl(CO)PN and IrCl(CO)PCN, where PN is *o*-(diphenylphosphino)-*N*,*N*-dimethylaniline and PCN is *o*-(diphenylphosphino)-*N*,*N*-dimethylbenzylamine, have been prepared. The compounds react with HCl and with a mixture of MeI and iodide to give $IrHCl_2(CO)PN$, $IrHCl_2(CO)PCN$, $IrMeI_2(CO)PN$, and $IrMeI_2(CO)PCN$. The relative order of effectiveness for the catalytic hydrogenation of hexene-1 is IrCl(CO)PCN > IrCl(CO)PN > $IrCl(CO)(PPh_3)_2$. The compound IrCl(CO)PCN is conformationally mobile because of inversion of the six-membered ring. Values for E_a, $\Delta H^\ddagger$, and $\Delta S^\ddagger$ are 18.0 kcal/mol, 17.5 kcal/mol, and 15.3 cal/(deg mol), respectively, which compare to values of 8.8 kcal/mol, 8.3 kcal/mol, and −17.4 cal/(deg mol) for RhCl(CO)PCN. Equilibrium measurements of [Ir(III)]/[Ir(I)] for the addition of benzoic acid to IrCl(CO)PCN, IrCl(CO)PN, and $IrCl(CO)(PPh_3)_2$ show that there is little difference in the basicities of the three metal centers. The compounds $IrCl(CO)(PCN)_2$ and $IrCl(CO)(PO)_2$ are also described, where PO is *o*-(diphenylphosphino)anisole.

Recently we have described the synthesis and chemistry of rhodium(I) complexes of *o*-(diphenylphosphino)-*N*,*N*-dimethylaniline (PN).[1] The stated purpose of this work was to prepare complexes of a low-valent metal where both the tertiary phosphine and the dimethylamino groups were coordinated to the metal. We considered at that time that these compounds could be of direct importance to homogeneous catalysis. The first consideration is that coordination of the amine can be anticipated to confer a high electron density on the central metal. In addition, since low-valent complexes are usually stabilized by π-acceptor ligands, we consider it likely that the coordinated dimethylamino group will undergo facile substitution by π-acceptor ligands. This facility of the dimethylamino group to be substituted by π-acceptor ligands has been demonstrated for the carbonylation of $[Rh(PN)_2]PF_6$, which is reversibly converted to $[Rh(PN)_2(CO)_2]PF_6$ by CO.[2] ^1H NMR spectroscopy was used in this case to verify that carbonylation proceeds by substitution of the dimethylamino group on rhodium, and the dicarbonyl complex was isolated and fully characterized.

In view of current mechanistic ideas on catalysis of addition reactions by transition metal d^8 compounds, it is apparent that electron-rich transition metal compounds having ligands which undergo facile displacement by π-acceptor ligands should be effective homogeneous catalysts for these reactions. Attempted hydrogenation of alkenes with $[Rh(PN)_2]PF_6$ was indecisive, however, since during the process small quantities of finely divided rhodium metal were formed. Since this material was found to be a highly active heterogeneous hydrogenation catalyst for alkenes, it was impossible to ascertain with any confidence the effectiveness of the complex as a hydrogenation catalyst. In order to prevent decomposition of the complex to the metal, it is necessary to use complexes where the metal–phosphorus bond is stronger. Since it is known that $IrCl(PPh_3)_3$, unlike $RhCl(PPh_3)_3$, does not undergo facile phosphine dissociation, it appeared likely that iridium(I) complexes of PN and PCN could be used to investigate whether these ligands would lead to compounds which were more highly active homogeneous catalysts.

The compound $IrCl(CO)(PPh_3)_2$ will catalyze the hydrogenation of alkene to alkane as a homogeneous solution in dimethylformamide. The mechanistic aspects of the reaction have been discussed by a number of authors, and there appears to be a body of evidence supporting the view that dissociation of triphenylphosphine is a critical step in the reaction sequence. Strohmeier et al. considered that an intermediate compound of the type $IrCl(CO)(PPh_3)_2$(olefin) is initially formed, which subsequently undergoes dissociation of triphenylphosphine.[3] James, in a study of the hydrogenation catalysis by $IrCl(CO)(PPh_3)_2$ in dimethylacetamide solution, has shown that the slow substitution of triphenylphosphine by dimethylacetamide is followed by a rapid substitution of the dimethylacetamide by the substrate, maleic acid, to be hydrogenated.[4] In agreement with these findings is the observation that the hydrogenation of terminal olefins by $IrCl(CO)(PPh_3)_2$ is inhibited by added phosphines.[5] Since the dissociation of triphenylphosphine from iridium(I) is not facile, it is to be anticipated that complexes IrCl(CO)PN and IrCl(CO)PCN, where dissociation of the dimethylamino group can occur quite readily, will be more effective than $IrCl(CO)(PPh_3)_2$ as hydrogenation catalysts.

Table I. Infrared and ^1H NMR Spectral Data for PN and PCN Complexes of Iridium[a]

Compd	τ_{Me}	τ_{CH_2}	ν_{CO}	Other bands
PN	7.41			
PCN	7.94	6.37		
PO	6.30			
IrCl(CO)PN	6.77		1950	295 ν_{IrCl}
IrCl(CO)PCN	7.46	6.39	1957	320 ν_{IrCl}
$IrCl(CO)(PCN)_2$	8.02	6.38	1960	319 ν_{IrCl}
$IrCl(CO)(PO)_2$	6.34		1925	
$IrHCl_2(CO)PN$	6.59, 6.28		2075	2230 ν_{IrH}
$IrHCl_2(CO)(PCN)$	7.39, 7.18	6.33, 6.22	2060	2230 ν_{IrH}
$IrMeI_2(CO)(PN)$	Insoluble		2045	
$IrMeI_2(CO)(PCN)$	Insoluble		2050	

[a] τ in ppm; ν in cm^{-1}.

Results and Discussion

The compounds chlorocarbonyl(*o*-(diphenylphosphino)-*N*,*N*-dimethylaniline)iridium(I), IrCl(CO)PN, and chlorocarbonyl(*o*-(diphenylphosphino)-*N*,*N*-dimethylbenzylamine)iridium(I), IrCl(CO)PCN, have been prepared by treating $Li[IrCl_2(CO)_2]$ with 1 equiv of the ligand PN or PCN (eq 1). The compounds are pale yellow and have a square-planar geometry with the dimethylamino group coordinated in iridium. Coordination of the dimethylamino group to iridium is verified by the ^1H NMR method discussed in some detail in our previous papers.[1,2,6] For the complex IrCl(CO)PN the resonance due to the methyl group is shifted downfield by 0.64 ppm from the position in free PN, and for

$$[IrCl_2(CO)_2]^- \begin{array}{l} \xrightarrow{PN} IrCl(CO)PN \\ \xrightarrow{PCN} IrCl(CO)PCN \end{array} \tag{1}$$

IrCl(CO)PCN the corresponding shift is 0.48 ppm (Table I). In the synthesis of these compounds care must be taken that excess ligand is not present. Since a tertiary phosphine coordinates much more strongly to iridium(I) than does a tertiary amine, the use of excess ligand leads to the formation of the four-coordinate complexes $IrCl(CO)(PN)_2$ and $IrCl(CO)(PCN)_2$. In a previous paper[6] we reported the synthesis of *o*-(diphenylphosphino)anisole (PO) and showed that it could act as a bidentate chelating ligand to Ru(II). We have tried unsuccessfully to prepare a similar complex of Ir(I); however in this case the only product isolated is $IrCl(CO)(PO)_2$, and the use of lesser quantities of PO simply results in a reduced yield of this same material.

The complexes IrCl(CO)PN and IrCl(CO)PCN oxidatively add HCl or a mixture of MeI and I^- to give $IrHCl_2(CO)PN$, $IrHCl_2(CO)PCN$, $IrMeI_2(CO)PN$, and $IrMeI_2(CO)PCN$. The hydro complexes can be readily isolated, even in the presence of excess HCl, without formation of the trichloro complex. Interestingly the addition of methyl iodide is quite different from what has been found for the analogous rhodium compounds. For iridium(III) carbonyls the alkyl is stable, whereas with the corresponding rhodium(III) compounds, the alkylcarbonyl is unstable to migratory insertion, and the product isolated from the reaction is the acyl. This observation appears to be general, in that oxidative addition of methyl iodide to monocarbonyliridium(I) compounds yields the methyl compound and to monocarbonylrhodium(I) compounds the acetyl complex.

The ^1H NMR spectrum of IrCl(CO)PCN shows single sharp lines for the methyl and methylene hydrogens at room temperature. Observation of models, however, indicates that the two methyl groups and the two methylene hydrogens should be mutually inequivalent, one being axial and one being equatorial, to the plane of the chelate ring. In an earlier study of the variable-temperature ^1H NMR spectrum of RhCl(CO)PCN, we concluded that at room temperature the methyl groups were undergoing rapid exchange by a mechanism involving twisting of the puckered ring.[6] At that time, however, we could not exclude the alternate mechanism involving dissociation of the amine, which could then undergo free rotation to mutually exchange the methyls and methylenes. We have now further investigated this conformationally nonrigid molecule in a range of solvents and compared the data with those now obtained for IrCl(CO)PCN. A dissociative mechanism could cause an exchange between the methyls and methylenes. This cannot be a slow rotation in the dissociated amine since the resonance does not center in the free ligand position, and the coalescence temperatures found for IrCl(CO)PCN and RhCl(CO)PCN differ by 15 °C. This means that the slow step in such a process must be directly involved with the dissociation or association step. We consider it very likely that such an explanation for the slow step of this process would necessitate that the rate of exchange be strongly solvent dependent. The variable-temperature ^1H NMR data for RhCl(CO)PCN previously reported were obtained in $CDCl_3$ solution, and we have now found that addition of a large excess of pyridine, CD_3CN, or CD_3COCD_3 to this solution causes no change in the coalescence temperature (250 K). Similarly we have obtained the coalescence temperature of the ^1H NMR spectrum of IrCl(CO)PCN in this same range of solvents, and found it to be 265 K in each case. These solvents have widely different coordinating power to d^8 metal centers, and we consider that these additional data eliminate a mechanism involving dissociation of the dimethylamino group from the metal. The observed and calculated ^1H NMR spectra for the methyl resonance over the temperature range of +10 to −18 °C are shown in Figure 1, and the Eyring plots from the line shape analysis are shown in Figures 2 and 3. In Tables II and III are shown the rate and temperature data obtained for RhCl(CO)PCN and IrCl(CO)PCN. The results give

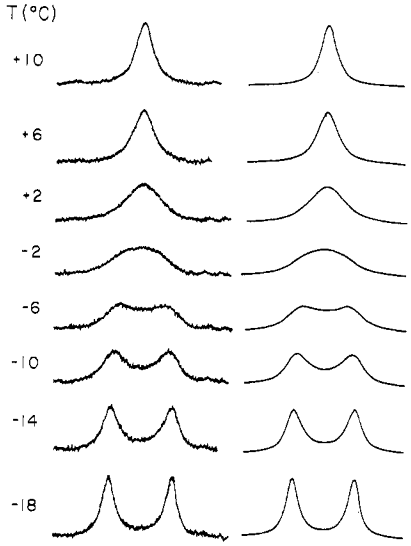


Figure 1. Observed and calculated spectra for IrCl(CO)PCN over the temperature range 283–255 K.

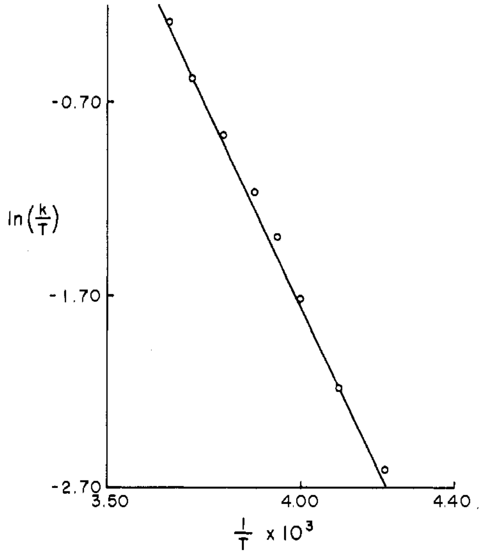


Figure 2. Eyring plot for RhCl(CO)PCN.

Table II. Kinetic Data for the Conformational Behavior of RhCl(CO)PCN

k, s^{-1}	T, K	$10^3/T$, K^{-1}	ln k	ln (k/T)
205	273.5	3.66	5.323	−0.287
150	268.5	3.72	5.011	−0.583
110	263.0	3.80	4.700	−0.872
80	258.0	3.88	4.382	−1.170
62.5	253.5	3.94	4.135	−1.401
45	250.0	4.00	3.807	−1.715
27.5	244.0	4.10	3.314	−2.183
17.5	237.0	4.22	2.862	−2.606

Table III. Kinetic Data for the Conformational Behavior of IrCl(CO)PCN

k, s^{-1}	T, K	$10^3/T$, K^{-1}	ln k	ln (k/T)
435	283	3.53	6.075	0.429
270	279	3.58	5.598	−0.034
150	275	3.64	5.011	−0.605
100	271	3.69	4.605	−0.997
61	267	3.75	4.111	−1.475
41	263	3.80	3.714	−1.859
21	259	3.86	3.045	−2.513
12	255	3.92	2.485	−3.057

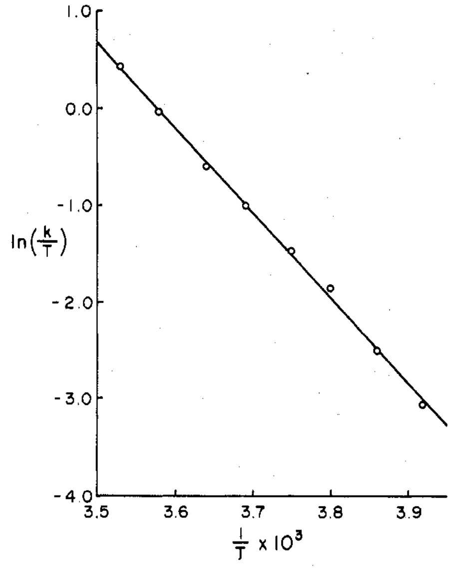
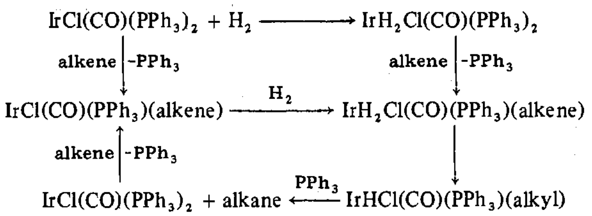


Figure 3. Eyring plot for IrCl(CO)PCN.

Scheme I



values for E_a, $\Delta H^‡$, $\Delta S^‡$, and $\Delta G^‡$ (263 K) of 18.0 kcal/mol, 17.5 kcal/mol, 15.3 cal/(deg mol), and 13.5 kcal/mol for IrCl(CO)PCN and values of 8.8 kcal/mol, 8.3 kcal/mol, −17.4 cal/(deg mol), and 12.9 kcal/mol, respectively, for RhCl(CO)PCN. It may be significant that the values for $\Delta G^‡$ are closely similar in each case; however it is an interesting observation that the values for $\Delta S^‡$ and $\Delta H^‡$ are very different, with the former having a different sign in the two cases. Earlier workers[7] have considered that the energetics of these inversions are related to the facility for forming a planar transition state, and our results show that this is strongly affected by size or bonding characteristics of charging the heteroatom in the ring.

The compound $IrCl(CO)(PPh_3)_2$ in donor solvents is effective for the hydrogenation of alkenes to alkanes at temperatures above ambient. Using dimethylformamide as solvent, with a pressure of hydrogen at 375 psig at 60 °C, we find that the yield of *n*-hexane from 1-hexene is 42% after 14 h. We have carried out this hydrogenation with IrCl(CO)PN and IrCl(CO)PCN under identical experimental conditions. The resulting yields of hexane are 54% for IrCl(CO)PN and 90% for IrCl(CO)PCN, showing that these mixed phosphine–amine complexes of iridium(I) have a significant advantage over the triphenylphosphine complex as a hydrogenation catalyst. Consideration of the mechanism (Scheme I) of catalytic hydrogenation by $IrCl(CO)(PPh_3)_2$ leads to the conclusion that the increased effectiveness of the phosphine–amine ligands could be due to the increased basicity of the ligand, smaller steric bulk, or the previously discussed facility for dissociation from the metal center. The first two effects should be apparent in an increased facility for compounds IrCl(CO)PN and IrCl(CO)PCN to undergo oxidative addition reactions, as compared to the facility of $IrCl(CO)(PPh_3)_2$. A previous study of the oxidative addition reaction of carboxylic acids to complexes of type *trans*-$IrX(CO)L_2$ has shown that the extent of protonation is dependent on the ligand L; the use of more basic and smaller phosphines such as PMe_2Ph causes a 100-fold increase in the iridium(III) compound as compared to PPh_3 as ligand.[8] The complex $IrCl(CO)(PPh_3)_2$ has an absorption band at 440 nm (ϵ 730), which shows a decrease in intensity upon addition of carboxylic acid. The change in intensity of this band upon addition of acid has been used to determine the position of the equilibrium. The complexes IrCl(CO)PN and IrCl(CO)PCN show bands at 385 nm (ϵ 2070 and 1830, respectively), and the ratio of [Ir(III)]/[Ir(I)] has been obtained similarly by plotting the change in absorption with time and extrapolating back to zero time. This method is identical with the one used by these previous authors.[8] The data obtained for the ratio [Ir(III)]/[Ir(I)] are as follows: $IrCl(CO)(PPh_3)_2$, 0.05 ± 0.02; IrCl(CO)PN, 0.04 ± 0.02; IrCl(CO)PCN, 0.05 ± 0.02. These results indicate that the use of these phosphine–amine ligands with iridium(I) does not increase the equilibrium concentration of the hydrocarboxylatoiridium(III) product. Previously[9] it has been shown that the equilibrium constant for hydrogen addition to iridium(I) complexes also correlates with ligand basicity; thus it is reasonable to assume that the equilibrium position for hydrogen addition will not be significantly different with the three compounds.

It appears unlikely therefore that steric or basicity effects are important in promoting the oxidative addition step in the catalytic cycle. The reason for the enhanced catalysis is at present not fully understood but it appears that increased facility for dissociation to give a coordinately unsaturated intermediate and promotion of the insertion step by the free amine may be significant factors.

Experimental Section

The compounds *o*-(diphenylphosphino)-*N*,*N*-dimethylaniline (PN), *o*-(diphenylphosphino)anisole (PO), *o*-(diphenylphosphino)-*N*,*N*-dimethylbenzylamine (PCN) were prepared as described previously.[6] Infrared spectra were recorded as Nujol mulls on a Perkin-Elmer Model 457 or 700 spectrometer. ^1H NMR spectra were measured on a Jeol MH 100 spectrometer as solutions in $CDCl_3$. $IrCl_3{\cdot}xH_2O$ was purchased from Engelhard Inc. Catalytic studies were carried out in a stainless steel autoclave fitted with a glass liner. The vessel was loaded with the iridium compound (0.1 mmol) and dimethylformamide (15 mL) was added. To this solution was added hexene-1 (1 mL), which had been passed through a short alumina column to remove peroxides. Cyclohexane (1 mL) was added as a GLC reference standard, and the reaction vessel pressured to 375 psig hydrogen. The hydrogenation was carried out for 14 h at 60 °C. The percent hexane was obtained by GLC using a silicone oil column. The reported data are the averages of six runs. Equilibrium measurements were made on a Cary 14 spectrophotometer using 1-cm cells. The concentration of the iridium(I) compound was 10^{-3} M, and the concentration of benzoic acid was 10^{-2} M. Data were obtained in benzene and dichloromethane, and the solutions were deoxygenated with N_2 prior to the addition of acid. The ^1H NMR line shape analysis was carried out using the DNMR-3 program.

Chlorocarbonyl(*o*-(diphenylphosphino)-*N*,*N*-dimethylaniline)iridium(I), IrCl(CO)PN. Carbon monoxide was bubbled through a stirred refluxing solution of $IrCl_3{\cdot}xH_2O$ (1.0 g) and LiCl (0.145 g) in 2-methoxyethanol (40 mL), until the color of the solution changed to straw yellow. The solution contained $Li[IrCl_2(CO)_2]$,[10] which was identified by the presence of bands at 1970 and 2056 cm^{-1} for ν_{CO} in the infrared stretching region. The carbon monoxide atmosphere was replaced by nitrogen, and PN (0.86 g), dissolved in a minimum volume of a mixture of CH_2Cl_2 and ethanol, was added. The stirred solution was allowed to cool for 2 h. The compound was filtered, washed with ethanol and then diethyl ether, and dried in vacuo. Recrystallization was carried out by dissolving the compound in CH_2Cl_2, adding ethanol, and then allowing the solution to slowly evaporate to give yellow crystals; yield 1.13 g (72%); mp 252–265 °C dec. Anal. Calcd for $C_{21}H_{20}ClIrONP$: C, 45.0; H, 3.57; N, 2.50. Found: C, 44.7; H, 3.59; N, 2.44.

Chlorocarbonyl(*o*-(diphenylphosphino)-*N*,*N*-dimethylbenzylamine)iridium(I), IrCl(CO)PCN. By use of a similar procedure with $IrCl_3{\cdot}xH_2O$ (1.31 g), LiCl (0.145 g), and PCN (1.182 g) the compound was obtained as yellow crystals; yield 1.76 g (86%); mp 220 °C dec.

Anal. Calcd for $\mathrm{C_{22}H_{22}ClIrONP}$: C, 46.0; H, 3.85; N, 2.44. Found: C, 45.9; H, 3.90; N, 2.36.

Chlorocarbonylbis(*o*-(diphenylphosphino)-*N*,*N*-dimethylbenzylamine)iridium(I), $\mathrm{IrCl(CO)(PCN)_2}$. The solution of $\mathrm{Li[IrCl_2(CO)_2]}$ was prepared as described above using $\mathrm{IrCl_3{\cdot}\mathit{x}H_2O}$ (0.063 g). An excess of PCN (>2 mol) was added to the solution, which was allowed to cool. The yellow solid was filtered, washed with ethanol and then diethyl ether, and dried in vacuo; yield 0.07 g (44%); mp 220 °C. Anal. Calcd for $\mathrm{C_{43}H_{44}ClIrN_2OP_2}$: C, 57.7; H, 4.96; N, 3.13. Found: C, 57.5; H, 4.91; N, 2.97.

Chlorocarbonylbis(*o*-(diphenylphosphino)anisole)iridium(I), $\mathrm{IrCl(CO)(PO)_2}$. The solution of $\mathrm{Li[IrCl_2(CO)_2]}$ was prepared using $\mathrm{IrCl_3{\cdot}\mathit{x}H_2O}$ (1.5 g) and LiCl (0.18 g). To this solution was added PO (2.44 g) and the hot solution allowed to cool. The yellow solid was filtered, washed with ethanol and then diethyl ether, and dried in vacuo; yield 2.72 g (77%); mp 237–240 °C dec. Anal. Calcd for $\mathrm{C_{39}H_{34}ClIrO_3P_2}$: C, 55.8; H, 4.08. Found: C, 55.3; H, 4.36.

Hydrodichlorocarbonyl(*o*-(diphenylphosphino)-*N*,*N*-dimethylaniline)iridium(III), $\mathrm{IrHCl_2(CO)PN}$. A suspension of IrCl(CO)PN (0.15 g) in ethanol was deoxygenated with a steady stream of nitrogen for 15 min. To the solution was added 6 M HCl (0.5 mL) and the solution stirred for 6 h under a nitrogen atmosphere. To the filtered solution was added hexane until the compound precipitated as a white solid. The compound was washed with diethyl ether and dried in air; yield 0.15 g (94%); mp 195–196 °C. Anal. Calcd for $\mathrm{C_{21}H_{21}Cl_2IrNPO}$: C, 42.4; H, 3.52; N, 2.34. Found: C, 42.0; H, 3.45; N, 2.30.

Hydrodichlorocarbonyl(*o*-(diphenylphosphino)-*N*,*N*-dimethylbenzylamine)iridium(III), $\mathrm{IrHCl_2(CO)PCN}$. By using a similar procedure for $\mathrm{IrHCl_2(CO)PN}$ the compound was prepared from IrCl(CO)PCN (0.115 g); yield 0.104 g (85%); dec pt >230 °C. Anal. Calcd for $\mathrm{C_{22}H_{23}Cl_2IrNPO}$: C, 43.2; H, 3.79; N, 2.29. Found: C, 42.9; H, 3.81; N, 2.29.

Methyldiiodocarbonyl(*o*-(diphenylphosphino)-*N*,*N*-dimethylaniline)iridium(III), $\mathrm{IrMeI_2(CO)PN}$. A solution of IrCl(CO)PN (0.2 g) and sodium iodide (0.7 g) was stirred in methanol, saturated with carbon monoxide, for 15 min. Methyl iodide (0.18 mL) was added, and the reaction mixture stirred for 45 min. The solvent was removed on a rotary evaporator and the residue extracted with dichloromethane (30 mL). Following filtration through Celite, ethanol (60 mL) was added, and the dichloromethane slowly removed. The complex was crystallized, filtered, washed with ethanol (3 × 5 mL) and diethyl ether (2 × 10 mL), and dried in vacuo. The fawn-colored compound showed a single spot on TLC using $\mathrm{CH_2Cl_2{-}(CH_3)_2CO}$ in the ratio 10:1; yield 0.2 g (71%); mp 225–230 °C dec. Anal. Calcd for $\mathrm{C_{22}H_{23}I_2IrNPO}$: C, 33.2; H, 2.90; N, 1.76. Found: C, 32.9; H, 2.83; N, 1.77.

Methyldiiodocarbonyl(*o*-(diphenylphosphino)-*N*,*N*-dimethylbenzylamine)iridium(III), $\mathrm{IrMeI_2(CO)PCN}$. The compound IrCl(CO)PCN (0.112 g) and sodium iodide (0.05 g) were suspended in oxygen-free acetone (20 mL). The solution was stirred for 30 min to complete the metathetical replacement. Carbon monoxide was bubbled through the solution and excess methyl iodide added. After stirring of the mixture for 30 min the volume of acetone was reduced to 1–2 mL, and hexane was added. The yellow-brown precipitate was filtered, washed with diethyl ether, and dried in air; yield 0.13 g (81%); mp >300 °C. Anal. Calcd for $\mathrm{C_{23}H_{25}I_2IrNPO}$: C, 34.2; H, 3.12; N, 1.73. Found: C, 34.1; H, 3.20; N, 1.68.

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Registry No. IrCl(CO)PN, 61483-21-4; IrCl(CO)PCN, 61483-22-5; $\mathrm{IrCl(CO)(PCN)_2}$, 61483-23-6; $\mathrm{IrCl(CO)(PO)_2}$, 61483-24-7; $\mathrm{IrHCl_2(CO)PN}$, 61483-25-8; $\mathrm{IrHCl_2(CO)(PCN)}$, 61483-26-9; $\mathrm{IrMeI_2(CO)(PN)}$, 61483-20-3; $\mathrm{IrMeI_2(CO)(PCN)}$, 61505-83-7; RhCl(CO)PCN, 53897-08-8; $\mathrm{Li[IrCl_2(CO)_2]}$, 55095-92-6; PN, 4358-50-3; PCN, 53881-33-7; PO, 53111-20-9.

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Preparation and Dynamic Properties of Some Dimeric Palladium(I) and Platinum(I) Complexes

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Substitution reactions of the dimers $\mathrm{[Pd_2(CNCH_3)_6](PF_6)_2}$, **1**, $\mathrm{[Pt_2(CNCH_3)_6](BF_4)_2}$, **2**, and $\mathrm{[PdPt(CNCH_3)_6](PF_6)_2}$, **3**, are described. Exchange of **1** or **2** with free methyl isocyanide is fast on a ^{1}H NMR time scale. Both *tert*-butyl isocyanide and phenyl isocyanide readily displace methyl isocyanide from **1** to produce $\mathrm{[Pd_2(CN\text{-}\mathit{t}\text{-}C_4H_9)_6](PF_6)_2}$ and $\mathrm{[Pd_2(CNC_6H_5)_6](PF_6)_2}$. Treatment of **1**, **2**, or **3** with triphenylphosphine in various ratios results in the isolation both mono- and bis(triphenylphosphine)-substituted complexes. Axial substitution by triphenylphosphine is preferred. The neutral complexes $\mathrm{Pd_2X_2(CNR)_4}$ (X = I, R = $\mathrm{CH_3}$, t-$\mathrm{C_4H_9}$, $\mathrm{C_6H_5}$; X = SCN, R = $\mathrm{CH_3}$) are formed by refluxing $\mathrm{[Pd_2(CNR)_6](PF_6)_2}$ with the halide or pseudohalide. These Pd(I) and Pt(I) complexes have been characterized by elemental analysis and infrared and proton magnetic resonance spectroscopy. Ionic complexes have also been characterized by solution conductivities. No reaction occurs between **1** and simple olefins or nitrogen donor ligands. Fluxional behavior has been found for $\mathrm{[Pd_2(CNCH_3)_6]^{2+}}$ and $\mathrm{[Pd_2(CNCH_3)_5\{P(C_6H_5)_3\}]^{2+}}$. These complexes have been studied in detail using line shape analysis techniques. The intramolecular rearrangement process for both molecules has been interpreted as involving a tetrahedral deformation about one metal center, rotation about the Pd–Pd bond, and a return to square-planar geometry. The activation parameters have been determined: for $\mathrm{[Pd_2(CNCH_3)_6]^{2+}}$, $\Delta G^{\ddagger} = 13.2$ kcal/mol; for $\mathrm{[Pd_2(CNCH_3)_5\{P(C_6H_5)_3\}]^{2+}}$, $\Delta G^{\ddagger} = 14.3$ kcal/mol.

Introduction

An increasing number of dimeric metal–metal bonded Pd(I) and Pt(I) complexes have been described within recent years.[1] Most of these M(I) species for which structural data are available contain bridging ligands. The preparation of the dimeric nonbridging isocyanide complexes **1**–**3** has been described recently.[2,3] A structural determination of the dipalladium complex **1** reveals two essentially square-planar