

of the cyclopentadienyl ring with respect to three iron-coordinated carbonyl ligands but also is in good agreement with semiempirical MO calculations carried out<sup>36</sup> on an idealized molecular configuration of *trans*-[Fe<sub>2</sub>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(CO)<sub>2</sub>(μ-CO)<sub>2</sub>]. Hence, the existence of both kinds of possible distortions of a cyclopentadienyl ring due to lack of cylindrical symmetry has now been experimentally established.

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**Registry No.** Co[η<sup>5</sup>-C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>](CO)<sub>2</sub>, 12129-77-0.

**Supplementary Material Available:** A listing of the observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

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## Synthetic, Structural, Stereochemical, and Catalytic Studies on Carbonyliridium(I) Complexes of *o*-(Diphenylphosphino)-*N,N*-dimethylaniline, *o*-(Diphenylphosphino)-*N,N*-dimethylbenzylamine, 2-(Diphenylphosphino)-*N,N*-dimethylethylamine, and 3-(Diphenylphosphino)-*N,N*-dimethylpropylamine

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The new complexes IrCl(CO)PEN and IrCl(CO)PPN have been prepared. The crystal structure of the complex IrCl(CO)PN shows a planar complex with chloride *trans* to the phosphine. The iridium-carbon bond (1.794 (7) Å) is short, and the iridium-phosphorus bond (2.197 (2) Å) is unusually short. These data are considered to be a consequence of the coordination of the  $\sigma$ -donor amine ligand. The iridium-nitrogen distance (2.180 (5) Å) is considered long. Integration of the data for  $\nu$ (Ir-Cl),  $\nu$ (IrC≡O), and  $\delta$ (<sup>31</sup>P) is used to conclude all the complexes have the same stereochemistry as IrCl(CO)PN. The complexes IrCl(CO)PN, IrCl(CO)PCN, and IrCl(CO)PEN are more effective than IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub> for the isomerization of 1-hexene under hydrogenation conditions.

### Introduction

Recently we have been interested in the coordination chemistry of unsymmetrical ligands with low-valent metal centers.<sup>1</sup> These ligands are chosen because they have an arylphosphine at one end to stabilize the metal ion in a low oxidation state and a weakly coordinating amine or ether function at the other end which will readily be substituted by an incoming  $\pi$ -acceptor ligand. In our previous article<sup>1d</sup> we describe the preparation and chemistry of the complexes IrCl(CO)PN and IrCl(CO)PCN. We now have extended this series to the complexes IrCl(CO)PEN and IrCl(CO)PPN using the compounds 2-(diphenylphosphino)-*N,N*-dimethylethylamine (PEN) and 3-(diphenylphosphino)-*N,N*-dimethylpropylamine (PPN)<sup>2</sup> (Figure 1). These latter compounds are of interest to us as ligands because the fully alkylated backbone between phosphorus and nitrogen should be more flexible for allowing the amine to become distant from iridium after substitution by a  $\pi$ -acceptor ligand.

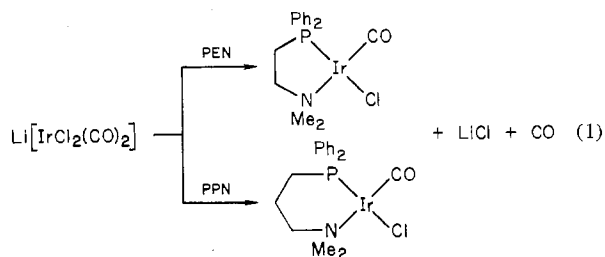
The compound IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub> will catalyze the hydrogenation of alkene to alkane as a homogeneous solution in dimethylformamide. The mechanistic aspects of the process have been discussed by a number of workers, and there appears to be a body of evidence supporting the view that dissociation of triphenylphosphine is a slow step in the catalytic sequence.<sup>3</sup> Since the dissociation of triphenylphosphine from iridium(I) is not particularly facile, this carbonyl-iridium(I) system

appeared to be a good one to test our ideas on the applications of these unsymmetrical ligands to homogeneous catalysis by low-valent transition-metal compounds.

In our previous articles, the assignment of stereochemistry to the new complexes with these ligands has been rather difficult. We decided therefore to solve the structure of the complex IrCl(CO)PN, and with the stereochemistry of one complex *known*, we can use this information to deduce the stereochemistries of similar complexes by spectroscopic methods.

### Results and Discussion

The complexes chlorocarbonyl(2-(diphenylphosphino)-*N,N*-dimethylethylamine)iridium(I), IrCl(CO)PEN, and chlorocarbonyl(3-(diphenylphosphino)-*N,N*-dimethylpropylamine)iridium(I), IrCl(CO)PPN, were prepared in a manner similar to IrCl(CO)PN and IrCl(CO)PCN by the addition of the appropriate ligand PEN or PPN to a solution of Li[IrCl<sub>2</sub>(CO)<sub>2</sub>] (eq 1).<sup>4</sup> The new complexes are air sensitive



- (1) (a) Rauchfuss, T. B.; Roundhill, D. M. *J. Organomet. Chem.* **1973**, *59*, C30-2. (b) Rauchfuss, T. B.; Roundhill, D. M. *J. Am. Chem. Soc.* **1974**, *96*, 3098-105. (c) Rauchfuss, T. B.; Patino, F. T.; Roundhill, D. M. *Inorg. Chem.* **1975**, *14*, 652-6. (d) Rauchfuss, T. B.; Clements, J. L.; Agnew, S. F.; Roundhill, D. M. *Inorg. Chem.* **1977**, *16*, 775-8. (2) (a) Knebel, W. I.; Angelici, R. J. *Inorg. Chim. Acta* **1973**, *7*, 713-6. (b) Taylor, R. C.; Walters, D. B. *Tetrahedron Lett.* **1972**, 63-6. (3) (a) Strohmeier, W.; Onoda, T. Z. *Naturforsch. B.* **1969**, *24*, 1217-9. (b) James, B. R.; Memon, N. A. *Can. J. Chem.* **1968**, *46*, 217-23. (c) James, B. R. "Homogeneous Hydrogenation"; Wiley: New York, 1973; Chapter XII.

and very soluble in a wide range of organic solvents. The complexes are primarily characterized by a carbonyl stretch band in the 1950 cm<sup>-1</sup> region. The infrared and NMR spectral data for these and related compounds are collected in Tables I and II. Other preparative routes beginning with [IrCl-

(4) Forster, D. *Inorg. Nucl. Chem. Lett.* **1969**, 433-6.

Table I. Infrared Spectral Data for the Ir and Rh Complexes

	$\nu(\text{MC}\equiv\text{O}),^a \text{ cm}^{-1}$	$\nu(\text{M}-\text{Cl}),^b \text{ cm}^{-1}$		$\nu(\text{MC}\equiv\text{O}),^a \text{ cm}^{-1}$	$\nu(\text{M}-\text{Cl}),^b \text{ cm}^{-1}$
IrCl(CO)PN	1973 (1950)	298	RhCl(CO)PN	2005	297
IrCl(CO)PCN	1980 (1975)	290	RhCl(CO)PCN	1991	293
IrCl(CO)PEN	1968 (1955)	300	RhCl(CO)dppe	2010	298, 282
IrCl(CO)PPN	(1950)		RhCl(PPh <sub>3</sub> ) <sub>3</sub>		299
IrCl(PPh <sub>3</sub> ) <sub>3</sub>		282			

<sup>a</sup> Solution in CH<sub>2</sub>Cl<sub>2</sub> (values in parentheses are in Nujol mull). <sup>b</sup> Vaseline mull.

Table II. NMR Spectra of the Ligands and Complexes as Solutions in Deuteriochloroform

	$\delta_{\text{Me}^-}$ ( <sup>1</sup> H) <sup>a</sup>	$\delta_{\text{P}}(^{31}\text{P})^b$	$J(^{31}\text{P}-^{103}\text{Rh})^d$	other
IrCl(CO)PN	3.23	31.0		
IrCl(CO)PCN	2.54			
IrCl(CO)PEN	2.70	35.2		
IrCl(CO)PPN	2.58			
RhCl(PPh <sub>3</sub> ) <sub>3</sub>		48.0, 31.5	189, 142	$J(^{31}\text{P}-^{31}\text{P}) = 38$
RhCl(CO)dppe		70.3, 49.1 <sup>c</sup>	158, 124	$J(^{31}\text{P}-^{31}\text{P}) = 34$
RhCl(CO)PN		56.9	168	
RhCl(CO)PCN		42.5	176	
PN	2.59	14.3		
PCN	2.06	15.6		
PEN	2.11	20.2		
PPN	2.16	16.5		

<sup>a</sup> Downfield shifts from Me<sub>4</sub>Si. <sup>b</sup> Downfield shifts from H<sub>3</sub>PO<sub>4</sub>.  
<sup>c</sup> Taken from ref 4a and converted to the H<sub>3</sub>PO<sub>4</sub> standard by the addition of the numerical value 112.5 ppm to the reported data.  
<sup>d</sup> In Hz.

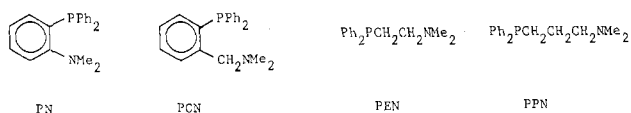


Figure 1. Structures and abbreviations of the ligands.

(cyclooctene)<sub>2</sub> or IrCl(CO)<sub>2</sub>(*p*-toluidine) give some success, but the preferred starting iridium complex is Li[IrCl<sub>2</sub>(CO)<sub>2</sub>].

**Description of Structure.** The compound IrCl(CO)PN crystallizes monoclinic with four molecules in the unit cell. The molecular structure shows a four-coordinate planar geometry about iridium. The compound is monomeric with the *o*-(diphenylphosphino)-*N,N*-dimethylaniline ligand chelated through both the phosphorus and nitrogen. The local stereochemistry about iridium(I) is shown in Figure 2 with the phosphorus trans to chloride and nitrogen trans to the carbonyl. The carbonyl ligand is close to linear about the carbon atom (Ir-C-O = 178.9 (6)°). The iridium(I)-phosphorus distance is very short, and the iridium(I)-nitrogen distance appears to be rather long. The iridium(I)-carbon bond is short, and the iridium(I)-chloride bond is close to accepted values. None of the other distances fall outside accepted ranges. The crystal data, atom positions and parameters, and bond lengths and angles are given in Tables III and IV. The ORTEP structure is shown in Figure 3.

The angles about iridium(I) show the coordination geometry of a distorted square. The angle P-Ir-N is 84.8 (1)° which shows that the ligand PN can closely accommodate the theoretical 90° bite angle. The angles about phosphorus and nitrogen approximate a tetrahedral arrangement. The methyl groups on the nitrogen are symmetrically placed above and below the coordination plane of the iridium.

The iridium(I)-phosphorus distance is sufficiently short that it falls below the accepted range for this bond. Churchill<sup>5</sup> in 1974 summarized the values for this bond distance for 23 cases and reported that they fell in the range 2.452 (9) to 2.248 (8) Å. We find this distance in the complex IrCl(CO)PN to be

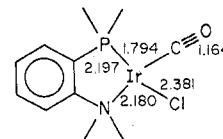


Figure 2. Stereochemistry and distances about iridium.

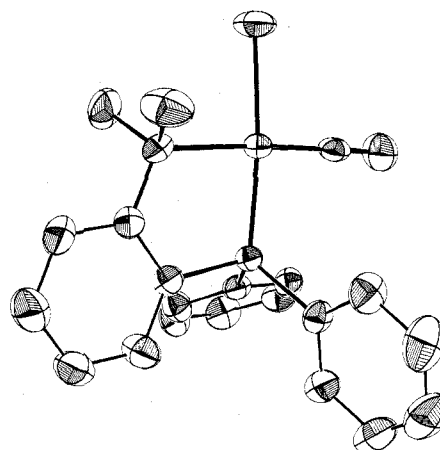


Figure 3. ORTEP drawing of the structure (50% probability ellipsoids).

2.197 (2) Å. It can be seen that this distance is considerably shorter than the minimum distance in the above range. Ranges of values have also been suggested for IrC≡O and Ir-C(O) distances in iridium(I) complexes. These respective ranges are 1.12 (2) to 1.20 (2) Å and 1.806 (18) to 1.939 (18) Å. We find these distances in IrCl(CO)PN to be 1.164 (8) Å and 1.794 (7) Å, respectively. Our distance for IrC≡O is not an unusual one, but again our found distance for Ir-C(O) falls below the minimum distance in the range suggested from other data. The iridium(I)-chloride bond distance in IrCl(CO)PN at 2.381 (2) Å is not an unusual one.

It is useful to make comparison between the structures of IrCl(CO)PN and *trans*-Ir(C<sub>6</sub>F<sub>5</sub>)CO(PPh<sub>3</sub>)<sub>2</sub>,<sup>6</sup> since in the former case one might anticipate the amine to donate electron density onto iridium(I) and in the latter case the C<sub>6</sub>F<sub>5</sub> group will withdraw electron density from the metal. The distances about iridium(I) are compared in Table V. The short Ir-P and Ir-C(O) distances in IrCl(CO)PN can be immediately recognized. We believe that this is of importance in trying to vary the electron density at iridium(I) by changing the nature of the coordinated ligands. In our earlier articles<sup>1</sup> we had suggested that the coordination of a primary amine, being solely a  $\sigma$ -donor ligand, may cause a significant increase in the electron density at iridium. Nevertheless in our previous article<sup>1d</sup> we measured the equilibrium constant for the addition of benzoic acid to IrCl(CO)PN and found little increase in basicity as compared to other iridium(I) complexes. We offered no explanation for the result at that time, but we believe this structural work gives a reason for such effects. Our data show that although the amine is directly coordinated to

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(6) Clearfield, A.; Gopal, R.; Bernal, I.; Moser, G. A.; Rausch, M. D. *Inorg. Chem.* **1975**, *14*, 2727-33.

Table III. Positional and Thermal Parameters for All Atoms in IrCl(CO)<sub>2</sub>PN

atom	x	y	z	B(1,1) or B	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)
Ir	0.295 54 (3)	0.129 16 (1)	0.187 08 (2)	0.007 44 (3)	0.001 71 (1)	0.004 05 (2)	-0.000 05 (1)	0.001 09 (1)	0.000 23 (1)
Cl	0.328 97 (21)	0.081 30 (12)	0.378 17 (15)	0.012 60 (26)	0.004 13 (8)	0.005 13 (13)	-0.001 40 (12)	-0.000 08 (15)	0.001 78 (8)
P	0.241 33 (17)	0.177 65 (9)	0.132 46 (13)	0.007 23 (19)	0.001 76 (5)	0.004 05 (11)	0.000 14 (8)	0.001 43 (12)	0.000 18 (6)
N	0.063 70 (57)	0.109 44 (30)	0.162 85 (43)	0.008 37 (66)	0.002 50 (19)	0.004 99 (39)	-0.000 22 (28)	0.002 54 (41)	0.000 50 (21)
C	0.484 46 (79)	0.146 97 (33)	0.197 69 (52)	0.011 85 (97)	0.001 78 (21)	0.004 48 (46)	0.001 02 (34)	0.001 43 (53)	0.000 74 (23)
O	0.606 60 (57)	0.159 71 (32)	0.204 75 (47)	0.009 05 (68)	0.004 18 (22)	0.009 89 (52)	-0.000 75 (32)	0.001 28 (47)	0.000 42 (27)
C(11)	0.278 67 (70)	0.274 00 (34)	0.008 95 (50)	0.009 31 (81)	0.001 89 (19)	0.004 19 (44)	0.000 16 (33)	0.001 90 (48)	0.000 26 (24)
C(12)	0.170 91 (78)	0.327 22 (40)	-0.001 30 (59)	0.009 37 (92)	0.002 35 (24)	0.006 56 (57)	0.000 48 (58)	0.000 72 (58)	-0.000 39 (30)
C(13)	0.209 93 (91)	0.399 24 (41)	0.006 92 (69)	0.012 46 (113)	0.002 05 (22)	0.009 26 (72)	0.001 11 (43)	0.001 66 (71)	-0.000 64 (33)
C(14)	0.350 67 (99)	0.419 97 (42)	0.027 13 (68)	0.016 94 (135)	0.001 90 (23)	0.008 46 (69)	-0.000 56 (47)	0.003 09 (76)	-0.000 54 (32)
C(15)	0.458 24 (85)	0.369 18 (45)	0.034 70 (61)	0.012 75 (101)	0.002 66 (24)	0.006 90 (56)	-0.001 44 (49)	0.002 00 (60)	0.000 41 (34)
C(16)	0.423 54 (77)	0.295 40 (39)	0.027 87 (60)	0.009 18 (88)	0.002 19 (22)	0.006 87 (57)	0.000 06 (36)	0.002 54 (57)	0.000 63 (29)
H(12)	0.063 78 (17)	0.313 96 (521)	-0.009 23 (756)	4.514 25					
H(13)	0.111 08 (06)	0.434 81 (520)	-0.004 18 (757)	4.977 84					
H(14)	0.381 65 (61)	0.475 91 (561)	0.033 09 (813)	5.247 56					
H(15)	0.556 07 (72)	0.381 42 (533)	0.051 18 (803)	4.814 87					
H(16)	0.495 18 (995)	0.261 19 (505)	0.029 26 (767)	4.086 76					
C(21)	0.312 90 (68)	0.139 84 (34)	-0.106 16 (52)	0.008 68 (76)	0.001 98 (22)	0.005 22 (46)	-0.000 07 (33)	0.001 73 (48)	-0.000 90 (25)
C(22)	0.361 16 (91)	0.068 78 (41)	-0.099 82 (71)	0.014 54 (117)	0.002 05 (24)	0.009 02 (72)	0.000 46 (44)	0.003 73 (76)	-0.000 08 (33)
C(23)	0.407 22 (112)	0.038 36 (52)	-0.194 05 (94)	0.019 87 (164)	0.002 91 (31)	0.013 78 (109)	0.000 83 (58)	0.006 46 (106)	-0.002 15 (49)
C(24)	0.405 82 (109)	0.077 36 (59)	-0.293 03 (79)	0.018 14 (153)	0.004 74 (42)	0.008 16 (80)	-0.001 17 (64)	0.003 86 (87)	-0.002 87 (48)
C(25)	0.359 92 (99)	0.147 69 (53)	-0.299 16 (66)	0.015 81 (124)	0.004 70 (40)	0.005 83 (61)	-0.001 23 (55)	0.003 94 (71)	-0.000 50 (37)
C(26)	0.313 04 (83)	0.179 83 (45)	-0.206 47 (60)	0.012 49 (106)	0.003 04 (27)	0.005 72 (55)	0.000 50 (44)	0.002 39 (61)	0.000 03 (32)
H(22)	0.365 49 (37)	0.040 27 (559)	-0.035 04 (813)	5.129 83					
H(23)	0.445 20 (88)	-0.013 02 (624)	-0.192 39 (932)	6.576 81					
H(24)	0.446 20 (67)	0.052 44 (608)	-0.350 27 (931)	6.576 81					
H(25)	0.369 49 (66)	0.175 88 (553)	-0.368 72 (852)	5.451 84					
H(26)	0.281 62 (66)	0.227 56 (547)	-0.213 79 (796)	4.691 63					
C(31)	0.046 81 (65)	0.166 28 (36)	-0.030 54 (51)	0.007 26 (74)	0.002 11 (20)	0.004 56 (45)	-0.000 62 (32)	0.001 08 (46)	-0.000 24 (25)
C(32)	-0.032 74 (82)	0.187 06 (43)	-0.138 78 (63)	0.010 66 (100)	0.002 87 (26)	0.006 79 (61)	-0.000 39 (41)	0.000 01 (61)	0.001 00 (32)
C(33)	-0.180 38 (86)	0.175 41 (49)	-0.167 05 (67)	0.010 96 (104)	0.004 09 (34)	0.006 75 (63)	-0.000 23 (49)	-0.000 20 (64)	0.001 15 (37)
C(34)	-0.249 80 (87)	0.144 93 (50)	-0.086 51 (73)	0.009 28 (96)	0.004 53 (38)	0.009 12 (74)	-0.000 76 (49)	-0.000 20 (68)	0.000 21 (41)
C(35)	-0.171 01 (74)	0.123 18 (50)	0.021 87 (64)	0.008 41 (84)	0.004 51 (34)	0.007 62 (60)	-0.000 14 (49)	0.003 21 (57)	0.000 16 (41)
C(36)	-0.022 21 (65)	0.132 54 (38)	0.048 10 (51)	0.007 67 (71)	0.002 37 (21)	0.005 24 (45)	0.000 23 (37)	0.001 31 (45)	-0.000 05 (29)
H(32)	0.012 44 (32)	0.213 58 (522)	-0.196 14 (764)	4.800 00					
H(33)	-0.239 79 (78)	0.195 55 (540)	-0.241 78 (848)	5.333 52					
H(34)	-0.358 91 (76)	0.130 07 (544)	-0.107 31 (881)	5.922 56					
H(35)	-0.218 91 (30)	0.100 80 (534)	0.809 94 (801)	5.107 80					
C(01)	0.041 11 (113)	0.029 29 (50)	0.176 43 (85)	0.016 44 (140)	0.003 16 (32)	0.009 95 (84)	-0.002 84 (55)	0.000 25 (87)	0.001 95 (41)
H(011)	0.067 14 (65)	0.005 24 (602)	0.112 41 (909)	5.870 98					
H(012)	-0.070 06 (84)	0.021 58 (568)	0.186 40 (850)	5.870 98					
H(013)	0.100 08 (16)	0.007 11 (561)	0.259 75 (934)	5.870 98					
C(02)	0.007 38 (98)	0.148 62 (63)	0.256 14 (72)	0.011 33 (114)	0.006 99 (53)	0.005 65 (59)	0.001 66 (63)	0.002 47 (66)	-0.001 63 (46)
H(021)	-0.107 31 (76)	0.131 71 (508)	0.241 61 (855)	6.588 29					
H(022)	0.069 36 (18)	0.137 92 (522)	0.341 13 (900)	5.688 29					
H(023)	0.032 44 (32)	0.197 24 (91)	0.259 19 (945)	5.688 29					

Table IV. Bond Distances (Å) and Angles (Deg) for IrCl(CO)PN

atoms	distance	atoms	angle
Nonring			
Ir-C	1.794 (7)	C-Ir-N	176.4 (2)
Ir-N	2.180 (5)	C-Ir-P	91.7 (2)
Ir-P	2.197 (2)	C-Ir-Cl	93.7 (2)
Ir-Cl	2.381 (2)	N-Ir-P	84.8 (1)
		N-Ir-Cl	89.8 (1)
		P-Ir-Cl	173.7 (1)
P-C(21)	1.823 (6)	C(21)-P-C(31)	104.4 (3)
P-C(31)	1.818 (6)	C(21)-P-C(11)	104.4 (3)
P-C(11)	1.821 (8)	C(21)-P-Ir	120.7 (2)
		C(31)-P-C(11)	107.2 (3)
		C(31)-P-Ir	104.4 (2)
		C(11)-P-Ir	114.8 (2)
N-C(36)	1.491 (8)	C(36)-N-C(02)	108.6 (5)
N-C(02)	1.500 (9)	C(36)-N-C(01)	108.4 (6)
N-C(01)	1.512 (10)	C(36)-N-Ir	114.6 (4)
		C(02)-N-C(01)	108.6 (7)
		C(02)-N-Ir	108.5 (5)
		C(01)-N-Ir	108.1 (5)
C-O	1.164 (8)	O-C-Ir	178.9 (6)
Ring 1			
C(11)-C(12)	1.404 (9)	C(16)-C(11)-P	117.5 (5)
C(12)-C(13)	1.382 (11)	C(12)-C(11)-P	123.3 (5)
C(13)-C(14)	1.357 (11)	C(16)-C(11)-C(12)	118.9 (6)
C(14)-C(15)	1.374 (11)	C(13)-C(12)-C(11)	119.5 (7)
C(15)-C(16)	1.403 (10)	C(14)-C(13)-C(12)	121.5 (7)
C(16)-C(11)	1.399 (9)	C(15)-C(14)-C(13)	120.2 (7)
		C(16)-C(15)-C(14)	120.1 (7)
		C(11)-C(16)-C(15)	119.6 (7)
Ring 2			
C(21)-C(22)	1.389 (9)	C(26)-C(21)-P	121.1 (5)
C(22)-C(23)	1.392 (11)	C(22)-C(21)-P	119.4 (5)
C(23)-C(24)	1.370 (14)	C(26)-C(21)-C(22)	119.4 (6)
C(24)-C(25)	1.370 (13)	C(23)-C(22)-C(21)	119.5 (8)
C(25)-C(26)	1.394 (10)	C(24)-C(23)-C(22)	121.1 (9)
C(26)-C(21)	1.395 (9)	C(25)-C(24)-C(23)	119.6 (8)
		C(26)-C(25)-C(24)	120.8 (8)
		C(21)-C(26)-C(25)	119.6 (8)
Ring 3			
C(31)-C(32)	1.396 (9)	C(36)-C(31)-P	116.6 (4)
C(32)-C(33)	1.383 (10)	C(32)-C(31)-P	123.6 (5)
C(33)-C(34)	1.380 (11)	C(35)-C(36)-N	120.4 (6)
C(34)-C(35)	1.400 (11)	C(31)-C(36)-N	119.5 (5)
C(35)-C(36)	1.387 (9)	C(36)-C(31)-C(32)	119.8 (6)
C(36)-C(31)	1.386 (8)	C(33)-C(32)-C(31)	120.3 (7)
		C(34)-C(33)-C(32)	119.7 (7)
		C(35)-C(34)-C(33)	120.5 (7)
		C(36)-C(35)-C(34)	119.5 (7)
		C(31)-C(36)-C(35)	120.1 (6)

Table V. Comparison of Distances (Å) to Iridium between IrCl(CO)PN and *trans*-Ir(C<sub>6</sub>F<sub>5</sub>)CO(PPh<sub>3</sub>)<sub>2</sub>

IrCl(CO)PN		<i>trans</i> -Ir(C <sub>6</sub> F <sub>5</sub> )CO(PPh <sub>3</sub> ) <sub>2</sub>	
Ir-P	2.197 (2)	Ir-P	2.326 (4), 2.305 (5)
Ir-C(O)	1.794 (7)	Ir-C(O)	1.891 (17)
Ir-Cl	2.381 (2)	Ir-C(σ)	2.090 (16)
Ir-N	2.180 (5)		

iridium(I), any electron density transferred from nitrogen to iridium apparently does not remain localized on the metal. Apparently this electron density is transferred to the phosphine and carbonyl ligands by a back-bonding  $\pi$  overlap leading to very short Ir-P and Ir-C(O) bonds. The observation that increasing the electron density at iridium leads to a shortening and presumably to a strengthening of these two bonds lends good credence to the concept that  $\pi$  metal to ligand overlap is a significant fraction of the bonding in complexes with metal ions in a low oxidation state.

The distance found for Ir-N appears to be rather long. There is no structure available for meaningful comparison, but a distance of 2.180 (5) Å does seem to be very close to the found Ir-P distance of 2.197 (2) Å. This lengthening cannot

be due to a trans-influence phenomenon, since, although it is known that the carbonyl ligand places high in the kinetic trans-effect series, it is nevertheless relatively low in the ground-state trans-influence ordering of ligands. We can only suggest that the long bond arises from the expected result<sup>1</sup> that a tertiary amine is a poorly coordinating ligand and particularly poor to a third-row transition metal in a low oxidation state. A similar long Ru-O distance has been found in the complexes *trans*- and *cis*-RuCl<sub>2</sub>(*o*-Ph<sub>2</sub>C<sub>6</sub>H<sub>4</sub>OMe)<sub>2</sub>.<sup>7</sup>

**Stereochemistry.** A consequence of using unsymmetrical chelate ligands rather than symmetrical phosphines is that more isomers are possible. The problem is easily recognizable but to date we have had only spectroscopic methods available to us to elucidate the structure obtained. With the solution to the structure of the complex IrCl(CO)PN, we are now in a position to compare the spectroscopic data from this complex with that of other complexes and to thereby make more sound decisions on their stereochemistries.

For the complexes IrCl(CO)L-L (L-L = PN, PCN, PEN, PPN) the dimethylamine group is coordinated to iridium(I). This has been shown by a characteristic shift of the methyl resonance in the <sup>1</sup>H NMR spectrum to lower field than is found in the free ligand. Comparison of the complexes IrCl(CO)L-L with these ligands gives the following downfield shifts, expressed as ppm: PN, 0.64; PCN, 0.48; PEN, 0.59; PPN, 0.42. These data show a similar magnitude of shift, and the direction always follows that expected for the amine behaving as a  $\sigma$  donor to the iridium.

The crystal structure of the complex IrCl(CO)PN confirms the monomeric state. This is a rather unique situation of carbonyliridium(I) complexes with bidentate ligands. Sanger has found that potentially chelating phosphine ligands give primarily dimeric complexes where the mutually trans-phosphine ligands span two metal centers.<sup>8</sup> This even occurs with 1,2-bis(diphenylphosphino)ethane (dppe) where the five-membered chelate ring monomer IrCl(CO)dppe is *not* formed. We believe that all the complexes IrCl(CO)L-L (L-L = Pn, PCN, PEN, PPN) are monomeric and have the stereochemistry found for IrCl(CO)PN. A dimeric complex with a bridge-spanning unsymmetrical ligand must necessarily have a symmetrical arrangement or we would not expect single bands for  $\nu$ (Ir-Cl) and  $\nu$ (IrC≡O). Such a structure would place the carbonyl and chloride, and also the phosphine and amine, in a mutually trans stereochemistry about each iridium. This would cause completely different trans pairs than is found with this, and from Tables I and II it is apparent that comparison between the the complexes IrCl(CO)L-L (L-L = PN, PCN, PEN) shows a close similarity for  $\nu$ (IrC≡O),  $\nu$ (Ir-Cl),  $\Delta\delta$ (Me), and  $\Delta\delta$ (<sup>31</sup>P). We therefore surmise that the three complexes are monomeric and have analogous stereochemistries. Nevertheless there is significant risk in making stereochemical assignments from spectral data since even slight differences between supposed comparable compounds can cause large shifts in spectral parameters. At point is the observed value of  $\nu$ (Ir-Cl) in IrCl(PPh<sub>3</sub>)<sub>3</sub>. From trans-influence arguments one would anticipate the value to be similar to that for IrCl(CO)PN, yet the found position is 282 cm<sup>-1</sup> rather than 298 cm<sup>-1</sup> for the latter (Table I).

The stereochemistry of the analogous rhodium complexes presents a similar problem. In an earlier article we suggested a stereochemistry for RhCl(CO)PN having the phosphorus trans to the carbonyl.<sup>1b</sup> This assignment was based on the close similarity of the values for  $\nu$ (RhC≡O) between RhCl(CO)PN

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and  $\text{RhCl}(\text{CO})\text{dppe}^9$  (Table I). We have now taken a closer look at this problem and have collected data on the  $^{31}\text{P}$  NMR spectra. The situation with respect to stereochemical determination by analysis of the  $\nu(\text{Rh}-\text{Cl})$  values is complicated by the fact that no clear assignment of  $\nu(\text{Rh}-\text{Cl})$  in  $\text{RhCl}(\text{CO})\text{dppe}$  can be made. For the complexes  $\text{RhCl}(\text{CO})\text{PN}$  and  $\text{RhCl}(\text{CO})\text{PCN}$ , the absorptions assigned to this stretch mode are at 297 and 293  $\text{cm}^{-1}$ . An excellent model compound for comparison of this mode in a known stereochemical environment is  $\text{RhCl}(\text{CO})\text{dppe}$ . Unfortunately a value for  $\nu(\text{Rh}-\text{Cl})$  with chloride trans to phosphine in this carbonylrhodium(I) complex cannot be definitively assigned because two strong bands are observed in the spectrum at 298 and 282  $\text{cm}^{-1}$ .<sup>8b</sup> This cannot be due to two symmetry allowed bands. Furthermore we have eliminated solid-state effects by observing the same spectrum with the complex dissolved in dibromomethane. Our only explanation for two bands is that neither is a pure rhodium-chloride mode. It is possible that a weak rhodium-phosphorus stretch mode is in the same region and that this mode for the phosphorus trans to chloride vibronically couples to the rhodium-chloride stretch and is intensity enhanced. If either of the bands is primarily of rhodium-chloride stretch character, it does not support our suggested stereochemistry with the phosphine trans to carbonyl.<sup>1b</sup> Assignment to 298  $\text{cm}^{-1}$  places the energy very close to the bands in  $\text{RhCl}(\text{CO})\text{PN}$  and  $\text{RhCl}(\text{CO})\text{PCN}$ , thereby suggesting the chloride and phosphine are mutually trans in these latter complexes. Assignment to 282  $\text{cm}^{-1}$  causes the chloride to be opposite a group of higher trans influence than a phosphine, and this assignment certainly does not support the amine and chloride mutually trans.

Our new  $^{31}\text{P}$  NMR data on these complexes support a stereochemistry with mutually trans phosphorus and chloride. In a detailed study of the  $^{31}\text{P}$  NMR spectrum of  $\text{RhCl}(\text{PPh}_3)_3$ , the phosphorus trans to chloride is assigned the line at  $\delta$  48.0 with  $^1J(^{31}\text{P}-^{103}\text{Rh}) = 189$  Hz, and the line at  $\delta$  31.5 with  $^1J(^{31}\text{P}-^{103}\text{Rh}) = 142$  Hz is due to the cis phosphorus.<sup>10</sup> These workers conclude that  $^1J(^{31}\text{P}-^{103}\text{Rh})$  is always larger for the phosphine trans to halogen. On the basis of this premise, we assign the line at  $\delta$  70.3 with  $^1J(^{31}\text{P}-^{103}\text{Rh}) = 158$  Hz in  $\text{RhCl}(\text{CO})\text{dppe}$  to the phosphorus trans to the chloride. This leaves the line at  $\delta$  49.1 with  $^1J(^{31}\text{P}-^{103}\text{Rh}) = 124$  Hz due to the phosphine cis to chloride. This assignment differs from that published previously<sup>8a</sup> but is logical assuming the conclusions in ref 10. These arguments lead to the conclusion that the respective values of 168 and 176 Hz for  $^1J(^{31}\text{P}-^{103}\text{Rh})$  in  $\text{RhCl}(\text{CO})\text{PN}$  and  $\text{RhCl}(\text{CO})\text{PCN}$  are large when compared to the values in  $\text{RhCl}(\text{PPh}_3)_3$  and  $\text{RhCl}(\text{CO})\text{dppe}$  and hence are representative of phosphines trans to chloride. We must conclude therefore that our initial suggestion on the stereochemistry of  $\text{RhCl}(\text{CO})\text{PN}$  is incorrect.

In conclusion, it appears that all these complexes have the stereochemistry with chloride and phosphorus mutually trans. This stereochemistry is reasonable on the basis of simple bonding arguments since it places the strongly  $\pi$ -acceptor carbonyl ligand opposite the amine ligand, which is solely a  $\sigma$ -donor group. If we assume that the orbitals bonding these mutually trans ligands will mix, this stereochemical arrangement best stabilizes both the carbonyl- and amine-iridium bonds.

#### Homogeneous Catalytic Hydrogenation and Isomerization.

In our previous article<sup>1d</sup> we describe some initial results on the use of these iridium(I) complexes as homogeneous hydrogenation catalysts. We have now extended these catalytic studies under more carefully controlled conditions and com-

Table VI. Percent of  $\text{C}_6$  Hydrocarbons Obtained after 16 h under Hydrogenation Conditions

complex	1-hexene	2-hexene	3-hexene	n-hexane
$\text{IrCl}(\text{CO})(\text{PPh}_3)_2$	36	9	14	41
$\text{IrCl}(\text{CO})\text{PN}$	12	21	30	37
$\text{IrCl}(\text{CO})\text{PCN}$	36	13	19	32
$\text{IrCl}(\text{CO})\text{PEN}$	13	22	33	32

pared the compounds as to their effectiveness as both hydrogenation and isomerization catalysts. The catalytic runs were carried out at 50  $^\circ\text{C}$ , a temperature at which there is negligible decomposition of the complex over a 16 h run. The solutions were purged with nitrogen prior to pressurizing with hydrogen, since previous workers have reported enhancement of the catalytic effects by the addition of oxygen.<sup>11</sup> This latter effect seems to be particularly significant for  $\text{IrCl}(\text{CO})\text{PCN}$  where it is difficult to obtain consistent results, and lack of care leads to the recovery of decomposed solutions. One additional effect can be ignored for our experimental conditions. Strohmeier has shown considerable photoenhancement of catalysis by iridium(I) complexes,<sup>12</sup> but since we are carrying out the catalysis in a stainless-steel autoclave, we cannot be observing such an acceleration. The data obtained for a series of iridium(I) carbonyl complexes under identical experimental conditions are shown in Table VI. These data show the effect of changing the complex through a series of ligands where it is progressively easier to dissociate a ligand from iridium. No further mechanistic features are implied since it is likely that there is a contribution from a free-radical pathway.<sup>13</sup>

From Table VI it is apparent that the iridium(I) complexes with the unsymmetrical chelate ligands show little effect on the yield of alkane. There is nevertheless a significant increase in the amount of isomerized olefin. In this respect the complexes  $\text{IrCl}(\text{CO})\text{PN}$  and  $\text{IrCl}(\text{CO})\text{PEN}$  are the most effective. At the end of a catalytic run using these complexes there is little hexene remaining as the 1-isomer, and a high proportion of 3-isomer is present in the solution. This facility for catalysis of isomerization by these complexes makes it difficult to make direct comparison of the relative effectiveness for olefin hydrogenation. It is well-known that internal olefins hydrogenate much more slowly than terminal olefins, so the low yield of n-hexane obtained with  $\text{IrCl}(\text{CO})\text{PN}$  and  $\text{IrCl}(\text{CO})\text{PEN}$  is partly due to the 1-hexene being converted into the 2- and 3-isomers.

Our comment about oxygen problems in obtaining data with  $\text{IrCl}(\text{CO})\text{PCN}$  comes partly from observations that dark colored solutions are recovered after catalysis. In addition we find that both  $\text{IrCl}(\text{CO})\text{PN}$  and  $\text{IrCl}(\text{CO})\text{PCN}$  react with oxygen at room temperature to give blue-green compounds. These compounds contain no carbonyl, and it is likely that the complexes are cationic chloride salts. Further work on this reaction with oxygen is in progress.

#### Experimental Section

The compounds *o*-(diphenylphosphino)-*N,N*-dimethylaniline (PN),<sup>14</sup> *o*-(diphenylphosphino)-*N,N*-dimethylbenzylamine (PCN),<sup>1</sup> 2-(diphenylphosphino)-*N,N*-dimethylethylamine (PEN),<sup>2</sup> and 3-(diphenylphosphino)-*N,N*-dimethylpropylamine (PPN)<sup>2</sup> were prepared as described previously. The complexes  $\text{IrCl}(\text{CO})\text{PN}$  and  $\text{IrCl}(\text{CO})\text{PCN}$  have been described previously.<sup>1</sup> The complexes  $\text{RhCl}-$

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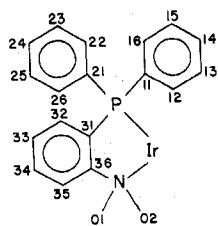


Figure 4. Numbering of the atom positions.

(CO)dppe<sup>6</sup> and IrCl(PPh<sub>3</sub>)<sub>3</sub><sup>15</sup> were prepared as described previously. Iridium trichloride hydrate was purchased from Engelhard, Inc., and Matthey Bishop, Inc. Infrared spectra in the carbonyl region were obtained as dichloromethane solutions on a Beckman IR4 prism instrument. Far-infrared spectra were measured as Vaseline mulls spread on a polyethylene sheet by using a Perkin-Elmer FIS3 spectrometer. <sup>1</sup>H NMR spectra were measured on a JEOL MH100 spectrometer as solutions in CDCl<sub>3</sub>. <sup>31</sup>P NMR spectra were measured at 35 °C on a Bruker WH90-FT spectrometer system as solutions in CDCl<sub>3</sub> in a 10-mm spinning sample tube.

Catalytic studies were carried out in a stainless-steel autoclave fitted with a glass liner. The vessel was loaded with the iridium complex (0.1 mmol) and DMF (10 mL) added. To this solution was added 1-hexene (1 mL) which had been previously passed through a short alumina column to remove peroxides. Cyclohexane (0.5 mL) was added as a GLC reference standard. The reaction vessel was purged with prepurified nitrogen and then pressurized to 350 psig with hydrogen. The reaction was stirred at 50 °C for 16 h. The percent hexane and hexenes were obtained by GLC using a silicone oil column, and the reported data are the average of several runs.

**Chlorocarbonyl(2-(diphenylphosphino)-*N,N*-dimethylethylamine)iridium(I), IrCl(CO)PEN.** To a mixture of IrCl<sub>3</sub>·xH<sub>2</sub>O (0.525 g; 1.46 mmol of Ir) and LiCl (0.062 g) was added deoxygenated ethanol (3 mL). The solution was heated to boiling for 15 min while the solution was purged with argon. The solution was then refluxed for 48 h under a stream of carbon monoxide. To the yellow solution was added PEN (0.376 g) and triethylamine (0.41 mL). The gas stream was changed back to argon and the solution cooled to -78 °C. The yellow complex precipitated. The compound was filtered cold (-78 °C), washed with a small quantity of ethanol and diethyl ether, and dried in vacuo at 56 °C; yield 0.215 g (29%). The complex can be recrystallized by the addition of ethanol to a filtered solution in dichloromethane at -78 °C. Anal. Calcd for C<sub>17</sub>H<sub>20</sub>ClIrONP: C, 39.8; H, 3.93; N, 2.73. Found: C, 39.6; H, 4.01; N, 2.67.

**Chlorocarbonyl(3-(diphenylphosphino)-*N,N*-dimethylpropylamine)iridium(I), IrCl(CO)PPN.** CH<sub>2</sub>Cl<sub>2</sub>. With a similar procedure as for IrCl(CO)PEN the very air-sensitive compound was obtained in low yield after recrystallization as the dichloromethane solvate. Anal. Calcd for C<sub>20</sub>H<sub>24</sub>Cl<sub>3</sub>IrONP: C, 37.5; H, 3.78; N, 2.19. Found: C, 38.2; H, 4.79; N, 2.46.  $\nu(\text{IrC}\equiv\text{O})$ : 1955 cm<sup>-1</sup> (KBr pellet).

**Crystal Structure Data.** A single-block-shaped crystal of dimension 0.2 mm was mounted on a glass fiber. Preliminary X-ray analysis showed that the crystal belonged to the *P*<sub>2</sub><sub>1</sub>/*n* space group because of systematic absences *0k0*, *k = 2n + l*, and *h0l*, *h + l = 2n + 1*. The final lattice constants were determined from least-squares refinement of the reciprocal lattice coordinates of 12 accurately centered reflections ( $\lambda_{\text{MoK}\alpha} = 0.71069 \text{ \AA}$ ) and are *a* = 9.4446 (14) Å, *b* = 18.5126 (40) Å, *c* = 11.7871 (17) Å, and  $\beta = 101.8^\circ$ . The calculated density for four formula units per unit cell is 1.799 g/cm<sup>3</sup>.

Intensity data were collected on an automated Picker full-circle diffractometer with Zr-filtered Mo K $\alpha$  radiation. A total of 4500

unique reflections were collected in the range  $4^\circ \leq 2\theta \leq 55^\circ$  using a  $\theta$ - $2\theta$  scan width of 2.2° with 20 steps/deg and 2 s/step. The reflections  $4^\circ \leq 2\theta \leq 15^\circ$  and  $15^\circ \leq 2\theta \leq 55^\circ$  were collected with two separate filters of approximate transmission ratio 3:1. Of the 4500 reflections, 3252 were regarded as "observed", i.e., with  $I \geq 5\sigma(I)$ . The standard deviation of each reflection was calculated by  $\sigma^2(I) = \text{TC} + \text{BG} + 0.03I^2$  where TC is the total counts, BG is background counts, and  $I = \text{TC} - \text{BG}$ . The intensities of three reflections were monitored every 20 reflections to check for decomposition, etc. These intensities did not decrease during data collection so no correction was applied to the recorded intensities.

**Structure Solution and Refinement.** Data were corrected for absorption ( $\mu = 72.39$ , transmission factors ranged from 0.32 to 0.43), and the position for the iridium atom was found from MULTAN and Patterson maps. The positions for other nonhydrogen atoms were found from MULTAN and Fourier mapping techniques. At the stage of refinement where all atoms were isotropic and only the iridium atom had variable thermal parameters, all nonhydrogen parameters converged to an *R* of 0.063 for reflections with  $F > 5\sigma$  and an *R<sub>w</sub>* of 0.065 where  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$  and  $R_w = [\sum w(|F_o| - |F_c|)^2]^{1/2} / \sum w|F_o|^2$ . Further refinement to the stage where all nonhydrogen atoms had refined thermal parameters, and Ir, Cl, P, N, C and O were anisotropic, led to an *R* of 0.040 and an *R<sub>w</sub>* of 0.040 on the 5 $\sigma$  data set. The goodness of fit was 1.465 with  $w = 1/\sigma^2(F)$ .

At this stage Fourier difference maps revealed the 20 hydrogen atoms, and they were inserted into the refinement with a thermal parameter one greater than the isotropic carbon to which they were bonded. These positions were fixed and all carbon atoms were allowed to refine anisotropically. Two cycles of refinement gave values ( $3\sigma$ ) for *R* = 0.041 and *R<sub>w</sub>* = 0.039, with a goodness of fit of 1.2350.

The parameter shifts on the last cycle were less than 2% of the value of their estimated error. Scattering factor tables for Ir, Cl, P, N, C, and O were taken from ref 16. Computer programs used are part of a local library.<sup>17</sup> Final parameters are listed in Table III and bond distances and angles are given in Table IV. The numbering system used is shown in Figure 4.

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**Registry No.** IrCl(CO)PEN, 72121-32-5; IrCl(CO)PPN, 72121-33-6; IrCl(CO)PN, 61483-21-4; IrCl(CO)PCN, 61483-22-5; IrCl(PPh<sub>3</sub>)<sub>3</sub>, 16070-58-9; RhCl(CO)PN, 52594-71-5; RhCl(CO)PCN, 53897-08-8; RhCl(CO)dppe, 15024-81-4; RhCl(PPh<sub>3</sub>)<sub>3</sub>, 14694-95-2; PN, 739-58-2; PCN, 53881-33-7; PEN, 29679-67-2; PPN, 961-04-6; IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub>, 59246-46-7; 1-hexene, 592-41-6; 2-hexene, 592-43-8; 3-hexene, 592-47-2; *n*-hexane, 110-54-3.

**Supplementary Material Available:** Tables of observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

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