these displacements give the molecule a pseudo-mirror-plane passing through Zr(1)Cl(11)Cl(13) and the C(11)-C(15) bond while for Zr(2) the result is a pseudo twofold axis passing through Zr(2) and the midpoint of the C(21)-C(25) bond. Clearly, there is sufficient flexibility in this molecule to accommodate both arrangements, and the structure uses both to give efficient molecular packing.

Acknowledgment. We are grateful to R. O. Wiley, J. E. Post, and J. J. Einck for many helpful discussions during the elucidation of these structures. We also acknowledge the generous allocation of computer time from the Arizona State University Academic Computer Services.

Registry No. $ZrCl_4(btz)$, 92315-30-5; $Zr(NCS)_4(bt)_2$, 92315-31-6; $ZrCl_4(bt)_2{\cdot}2CH_3CN$, 92315-33-8.

Supplementary Material Available: Unit cell diagrams and listings of calculated hydrogen positions, anisotropic thermal parameters, and observed and calculated structure factor amplitudes (95 pages). Ordering information is given on any current masthead page.

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2,6-Bis(diphenylphosphino)pyridine as a Bridging Ligand in Planar Complexes of Platinum(II) and Palladium(II)

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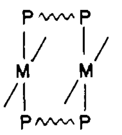
The reactions between 2,6-bis(diphenylphosphino)pyridine and (1,5-cyclooctadiene)MX_2 (M = Pd or Pt; X = Cl, Br, or I) have been studied by $^{31}P\{^1H\}$ NMR spectroscopy and product isolation. With palladium *cis,cis,trans*-$Pd_3[\mu\text{-}(Ph_2P)_2py]_3Cl_6$ forms in high yield and is remarkably stable toward conversion to other isomers or polymeric forms. With platinum, complex mixtures form from which pure compounds can be separated. The structures of two of these have been determined by X-ray diffraction. *cis,cis*-$Pt_2[\mu\text{-}(Ph_2P)_2py]_2Cl_4{\cdot}6CH_2Cl_2$ crystallizes in the space group $P2_1/c$ (No. 14) with cell dimensions (at 140 K) a = 16.17 (4) Å, b = 14.60 (4) Å, c = 16.36 (5) Å, β = 110.9 (2)°, and Z = 2. The structure was refined to R = 0.066 for 3005 reflections and 465 parameters. *trans,trans*-$Pt_2[\mu\text{-}(Ph_2P)_2py]_2I_4{\cdot}2CH_2Cl_2$ crystallizes in the space group $C2/c$ (No. 15) with unit cell dimensions (at 140 K) a = 24.093 (7) Å, b = 21.544 (6) Å, c = 12.287 (3) Å, β = 95.08 (2)°, and Z = 4. The structure was refined to R = 0.056 for 3102 reflections and 325 parameters.

Introduction

Bidentate phosphines have proven to be useful in constructing binuclear complexes that can have a variety of interactions between the two metal centers.[2] Study of the binding of small molecules to the cavity between the two metals in these binuclear complexes continues to attract attention.[3] In exploring these binuclear complexes, it is important to establish the range of structural types available and to determine the factors controlling their formation.

For binuclear complexes, the face-to-face structure **1** represents a now rather common structural type for molecules containing two square-planar metal ions. A number of examples have been structurally characterized.[4-9] With a bis(phosphine) like 2,6-bis(diphenylphosphino)pyridine, $(Ph_2P)_2py$, the formation of such a structure would produce a cavity between the two metal atoms where small molecules and even other metal ions could be bound by a combination of the nucleophilic pyridine nitrogens and the amphoteric metal centers. The rigid nature of $(Ph_2P)_2py$ precludes the formation of a chelate ring with both phosphorus atoms coordinated to a single metal atom.[10-12] This, however, does not ensure that structure **2** will readily form. Mixing $(Ph_2P)_2py$ with (cyclooctadiene)palladium(II) dichloride gives the remarkable trinuclear complex **3** in high yield.[13] This complex contains



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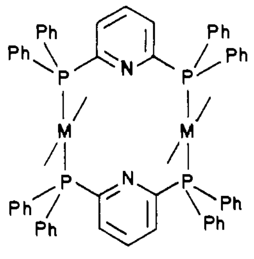

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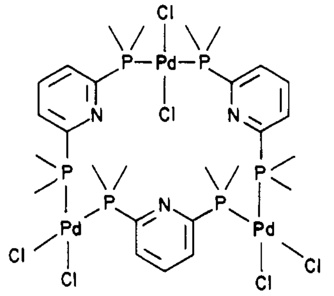

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[1] Permanent address: Department of Chemistry, University of Oslo, Blindern, Oslo 3, Norway.

[2] (a) Balch, A. L. In "Homogeneous Catalyses with Metal Phosphine Complexes"; Pignolet, L. H., Ed.; Plenum Press: New York, in press. (b) Balch, A. L. In "Reactivity of Metal-Metal Bonds"; Chisholm, M. H., Ed.; American Chemical Society: Washington, DC, 1981; ACS Symp. Ser. No. 155, p 167. (c) Puddephatt, R. J. In "Reactivity of Metal-Metal Bonds"; Chisholm, M. H., Ed.; American Chemical Society: Washington DC, 1981; ACS Symp. Ser. No. 155, p 187. (d) Balch, A. L. In "Catalytic Aspects of Metal Phosphine Complexes"; Alyea, E. C.; Meek, D. W., Eds.; American Chemical Society: Washington DC, 1982; ACS Symp. Ser. No. 196, p 243.

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[10] However, chelation via a phosphorus/nitrogen pair similar to that found for the related ligand 2-(diphenylphosphino)pyridine does remain a distinct possibility for coordination of $(Ph_2P)_2py$.

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[12] Farr, J. P.; Olmstead, M. M.; Wood, F. E.; Balch, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 792.

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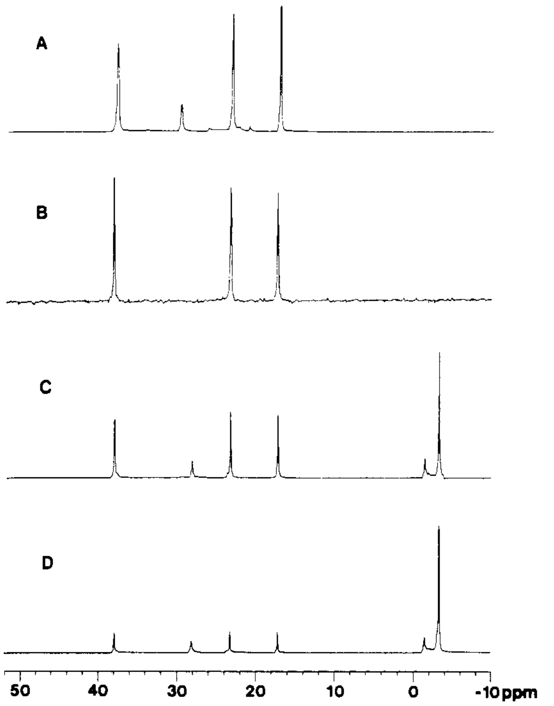
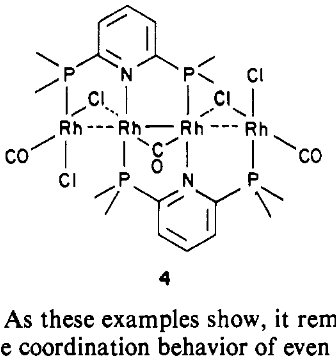


Figure 1. $^{31}P\{^1H\}$ NMR spectra of the $Pd/(Ph_2P)_2py/Cl$ system: (A) solution of equimolar quantities of $(COD)PdCl_2$ and $(Ph_2P)_2py$ in chloroform (note the trimeric compound $Pd_3[\mu\text{-}(Ph_2P)_2py]_3Cl_6$ is already the predominant species); (B) dichloromethane solution of the purified product $Pd_3[\mu\text{-}(Ph_2P)_2py]_3Cl_6$; (C) dichloromethane solution resulting from the addition of a moderate excess of $(Ph_2P)_2Py$ (49 mg, 0.110 mmol) to the trimeric compound (48 mg, 0.0256 mmol); (D) large excess of $(Ph_2P)_2py$ (97 mg, 0.217 mmol) added to $Pd_3[\mu\text{-}(Ph_2P)_2py]_3Cl_6$ (48 mg, 0.0256 mmol) in dichloromethane.

two distinct types of palladium ions (two with cis stereochemistry, one with trans) and is quite stable with regard to changes in ring size and palladium stereochemistry. Treatment of $(Ph_2P)_2py$ with dicarbonylrhodium(I) chloride dimer yields the tetranuclear complex **4**,[13] which has been converted into **5** by treatment with carbon monoxide in methanolic solution.[14]



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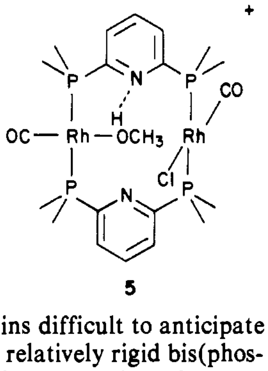

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As these examples show, it remains difficult to anticipate the coordination behavior of even a relatively rigid bis(phosphine) ligand. Here we report on further studies of the coordination of this ligand to simple palladium(II) and platinum(II) halo complexes.

Results

Preparative Studies. We have examined the reactions between $(Ph_2P)_2py$ and simple palladium(II) or platinum(II) halo complexes by monitoring $^{31}P\{^1H\}$ NMR spectra throughout the course of the reaction and by isolating and characterizing homogeneous samples of products. Figure 1 shows some $^{31}P\{^1H\}$ NMR data relating to the formation and stability of **3**. Trace A shows the $^{31}P\{^1H\}$ NMR spectrum of a solution of equimolar amounts of (1,5-cyclooctadiene)palladium(II) chloride, $(COD)PdCl_2$, and $(Ph_2P)_2py$ within 5 min after mixing. The three peaks of **3**, which may be isolated from such a solution and has been purified, are readily apparent. They appear again in trace B, which shows the spectrum obtained from redissolving a purified sample. Although P–P coupling of the nonequivalent, cis phosphine ligands might be expected, it is not observed and must be less than the natural line width (5 Hz). In trace A the other peaks present must result from other unidentified palladium complexes that are either isomers of **3** or molecules with different degrees of polymerization. No free $(Ph_2P)_2py$ is indicated in trace A, and clearly **3** is formed in high yield. The chemical shift data from the $^{31}P\{^1H\}$ NMR spectra of these and other relevant compounds are collected in Table I.

Table I. $^{31}P\{^1H\}$ NMR Parameters

compd	δ	^1J(Pt,P), Hz
cis,cis,trans-$Pd_3[\mu\text{-}(Ph_2P)_2py]_3Cl_6$ (**3**)	37.8, 23.1, 17.1	
$Pd[(Ph_2P)_2py]_2Cl_2$	28.0, −1.6	
cis,cis,trans-$Pd_3[\mu\text{-}(Ph_2P)_2py]_3Br_6$	36.4, 19.9, 14.7	
$[Pd((Ph_2P)_2py)Br_2]_n$	18.1	
cis,cis-$Pt_2[\mu\text{-}(Ph_2P)_2py]_2Cl_4$ (**6**)	9.9	3689
$[Pt_2((Ph_2P)_2py)Cl_2]_n$ (**7**)	14.3	3647
trans,trans-$Pt_2[\mu\text{-}(Ph_2P)_2py]_2I_4$ (**8**)	6.2	2595
$(Ph_2P)_2py$	−3.4	

The trimer **3** shows a remarkable degree of stability. The complex has been heated for 5 days at 132 °C in chlorobenzene solution. No change was detected in the $^{31}P\{^1H\}$ NMR spectra during that period. Solutions of **3** were treated with urea or *tert*-butylamine hydrochloride in order to see if hydrogen bond donors might bind to the cavity of this complex through the pyridine nitrogen atoms. We hoped that this might alter the structure so that one of the other three isomers (cis,cis,cis, trans,trans,trans, or cis,trans,trans) would be favored and might form. However, no change in the $^{31}P\{^1H\}$ NMR spectrum was observed immediately upon addition of these two species or within 8 h after addition. Finally, the effect of additional $(Ph_2P)_2py$ on **3** was examined. The addition of small quantities of $(Ph_2P)_2py$ was expected to catalyze any thermodynamically favored isomerization by providing means for an associative path for isomerization to occur. The effect of addition of free ligand is seen in traces C and D of Figure 1. Three new peaks appear in the spectrum. The one at −3.43 ppm is due to uncomplexed $(Ph_2P)_2py$ while the resonances at 28.00 and −1.6 ppm are assigned to $Pd[(Ph_2P)_2py]_2Cl_2$, which is believed to have two monodentate phosphine ligands. The low-field resonance is ascribed to the coordinated phosphorus while the high-field resonance is assigned to the uncoordinated phosphorus. The intensities of these two resonances are equal under all conditions, and the intensity data for all resonances indicate that the equilibrium expressed by eq 1 is established in dichloromethane solution. At 21.0 °C the equilibrium constant for eq 1 is 3.5×10^{-4}. It is remarkable that the 18-membered ring in **3** can be equilibrated with a monomeric compound while detectable quantities of other isomers or polymers are not formed. This must be a consequence of the thermodynamic stability of **3** over all other isomers or other polymeric forms.

$$Pd_3[\mu\text{-}(Ph_2P)_2py]_3Cl_6 + 3(Ph_2P)_2py \rightleftharpoons 3Pd[(Ph_2P)_2py]_2Cl_2 \quad (1)$$

Using bis(benzonitrile)palladium(II) chloride rather than $(COD)PdCl_2$ as the source of palladium(II) also produces **3** in high yeild.

The reaction between $(COD)PdBr_2$ and $(Ph_2P)_2py$ in 1:1 molar ratio has also been examined by $^{31}P\{^1H\}$ NMR spec-

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(13) Wood, F. E.; Olmstead, M. M.; Balch, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 6332.

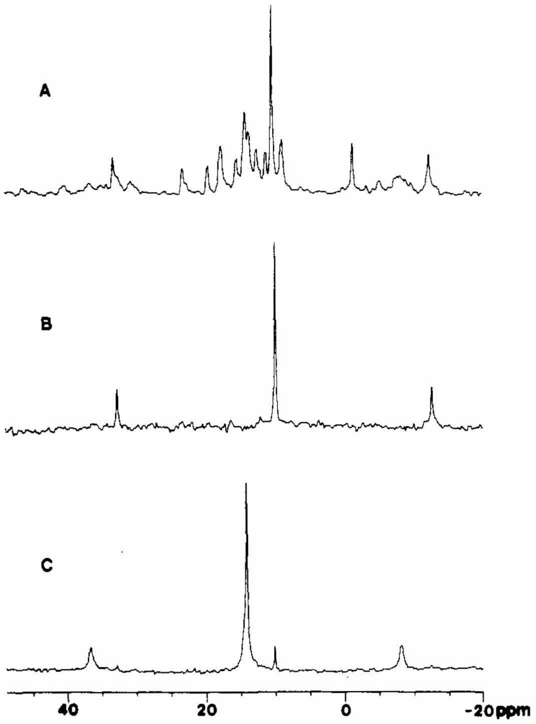

Figure 2. $^{31}P\{^1H\}$ NMR spectra of the Pt/$(Ph_2P)_2py$/Cl system: (A) dichloromethane solution of equimolar quantities of $(Ph_2P)_2py$ and $(COD)PtCl_2$; (B) dichloromethane solution of purified *cis,cis*-$Pt_2[\mu\text{-}(Ph_2P)_2py]_2Cl_4$; (C) dichloromethane solution of the white precipitate **7**, formed by quickly treating the initial mixture with diethyl ether.

troscopy. Upon mixing, a stable dichloromethane solution is formed. Its ^{31}P NMR spectrum indicates that two species are present. Three resonances of equal intensity are presumed to be due to the presence of the bromo analogue of **3**, although the cis,trans,trans isomer could also produce this pattern. A singlet at 18.0 ppm is due to some other palladium complex, which has not been isolated, so its structure is unknown. The ratio of the amount of this unknown material to that of the trimer is 1:7.

The reactions between $(Ph_2P)_2py$ and platinum(II) complexes produce more complex mixtures than those observed from palladium(II) compounds, and these mixtures only slowly equilibrate over a period of days. The $^{31}P\{^1H\}$ NMR spectrum of the solution obtained by adding $(Ph_2P)_2py$ to $(COD)PtCl_2$ in chloroform is shown in trace A of Figure 2. This spectrum was obtained within 20 min of mixing. While a number of species are present, all of the $(Ph_2P)_2py$ has reacted as shown by the absence of a resonance at −3.4 ppm. When the order of addition of the two reagents is reversed, the same resonances are present but the relative intensities differ. Two of the species present in this mixture have been isolated. By allowing the mixture to stand for periods of up to 1 week, well-formed colorless crystals of a homogeneous species, **6**, separate. The $^{31}P\{^1H\}$ NMR spectrum of **6** is shown in trace B of Figure 2. The magnitude of $^1J(Pt,P)$ in this spectrum is consistent with a structure with phosphorus trans to chloride, rather than trans to phosphorus.[15] The compound, unfortunately, has very low solubility, which limits exploration of its chemical reactivity. However, because the crystals of **6** were available, it was possible to establish from an X-ray diffraction study that they contained a cis,cis dimer that is described in the next section. By adding ethyl ether to a freshly prepared mixture of $(COD)PtCl_2$ and $(Ph_2P)_2py$ in chloroform, it is possible to separate a second, colorless substance, **7**. Its $^{31}P\{^1H\}$ NMR spectrum is shown in trace C of Figure 2. Again, the magnitude of $^1J(P,Pt)$ indicates that the phosphorus atoms are trans to chloride ligands rather than phosphorus ligands.[15] This complex is unstable, and in dichloromethane solution it undergoes rearrangement to form the cis,cis dimer **6** within 1 h.

Table II. Atom Coordinates (×10^4) and Temperature Factors (Å^2 × 10^{-3}) for $Pt_2[\mu\text{-}(Ph_2P)_2py]_2Cl_4 \cdot 6CH_2Cl_2$

atom	*x*	*y*	*z*	U^a
Pt	3444 (1)	2043 (1)	406 (1)	30 (1)
Cl(1)	2120 (3)	2698 (3)	−550 (3)	38 (2)
Cl(2)	3653 (4)	3367 (3)	1289 (3)	39 (2)
P(1)	3222 (4)	836 (3)	−505 (3)	31 (2)
P(2)	4642 (4)	1451 (3)	1488 (3)	32 (2)
N	4411 (10)	−181 (8)	−976 (9)	29 (6)
C(11)	4188 (13)	686 (10)	−823 (11)	32 (8)
C(12)	4557 (13)	1447 (11)	−1029 (11)	32 (8)
C(13)	5199 (14)	1344 (11)	−1449 (13)	42 (9)
C(14)	5381 (12)	480 (10)	−1659 (11)	27 (7)
C(15)	4991 (14)	265 (12)	1377 (12)	39 (9)
C(21)	2326 (13)	886 (10)	−1566 (12)	35 (9)
C(22)	2454 (14)	1249 (11)	−2307 (12)	37 (9)
C(23)	1755 (14)	1256 (13)	−3110 (11)	45 (9)
C(24)	913 (12)	916 (12)	−3191 (14)	44 (9)
C(25)	800 (15)	566 (13)	−2453 (13)	46 (10)
C(26)	1477 (15)	531 (13)	−1670 (14)	48 (10)
C(31)	2928 (12)	201 (11)	−27 (10)	25 (7)
C(32)	3012 (13)	−1071 (11)	−338 (11)	36 (8)
C(33)	2694 (14)	−1781 (14)	−26 (12)	44 (9)
C(34)	2322 (15)	−1698 (13)	593 (12)	47 (10)
C(35)	2225 (13)	−803 (11)	900 (12)	34 (8)
C(36)	2511 (13)	−71 (12)	547 (12)	38 (9)
C(41)	4405 (13)	1329 (10)	2495 (12)	33 (8)
C(42)	3561 (14)	1475 (11)	2489 (14)	40 (9)
C(43)	3367 (14)	1327 (11)	3264 (14)	46 (10)
C(44)	4019 (13)	1018 (11)	3972 (13)	41 (9)
C(45)	4878 (16)	886 (12)	4044 (13)	50 (10)
C(46)	5035 (14)	1041 (12)	3280 (12)	43 (9)
C(51)	5684 (13)	2048 (11)	1731 (11)	35 (8)
C(52)	6501 (13)	1673 (12)	2256 (12)	35 (8)
C(53)	7290 (13)	2109 (12)	2406 (12)	34 (8)
C(54)	7313 (14)	2965 (13)	2021 (12)	46 (9)
C(55)	6512 (14)	3352 (12)	1512 (13)	47 (10)
C(56)	5724 (13)	2916 (12)	1372 (11)	38 (8)
C(1)	489 (17)	3226 (15)	7309 (13)	59 (11)
Cl(3)	−633 (4)	2991 (4)	6678 (4)	68 (3)
Cl(4)	961 (5)	3909 (4)	6682 (4)	77 (3)
C(2)	93 (19)	2465 (17)	4681 (14)	64 (12)
Cl(5)	−285 (4)	1350 (4)	4241 (4)	66 (3)
Cl(6)	−224 (5)	3297 (4)	3853 (5)	77 (3)
C(3)	1886 (17)	4932 (13)	9946 (16)	59 (12)
Cl(7)	1612 (4)	5194 (4)	8802 (4)	65 (3)
Cl(8)	2549 (5)	5819 (4)	10593 (4)	75 (3)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

The reaction between $(Ph_2P)_2py$ and $(COD)PtI_2$ similarly produces a complex mixture. One species, **8**, with a major peak at 6.25 ppm and satellites showing $^1J(P,Pt)$ of 2595 Hz, is readily distinguishable while a complex, broad resonance centered at 12 ppm also appears to have satellites due to coupling with ^{195}Pt. No free $(Ph_2P)_2py$ is present. On standing, orange crystals of **8** are deposited. Redissolving these gives the ^{31}P nMR spectral parameters of **8**. An X-ray diffraction study (vide infra) has shown that these crystals contain a trans,trans dimer; i.e., **2** with X = I, M = Pt has formed. The magnitude of $^1J(P,Pt)$ is consistent with trans stereochemistry for the PtI_2P_2 unit.[15]

The Solid-State Structure of 6, $Pt_2[\mu\text{-}(Ph_2P)_2py]_2Cl_4 \cdot 6CH_2Cl_2$. In the solid state this compound adopts a structure involving a central 12-membered ring arranged about a center of symmetry in the unit cell. A drawing of the complex, along

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(14) Wood, F. E.; Hvoslef, J.; Balch, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 6986.

(15) Pregosin, P. S.; Kunz, R. W. *NMR: Basic Princ. Prog.* **1979**, *16*, 94.

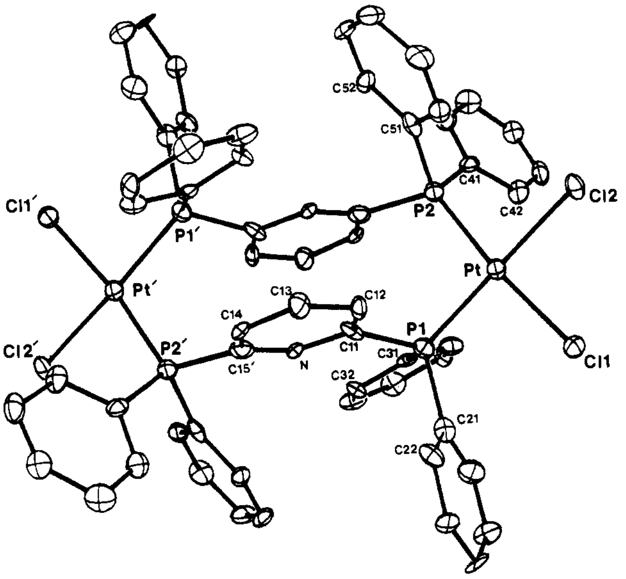

Figure 3. Perspective drawing of $Pt_2[\mu\text{-}(Ph_2P)_2py]_2Cl_4$ drawn using 40% thermal ellipsoids.

Table III. Molecular Dimensions for $Pt_2[\mu\text{-}(Ph_2P)_2py]_2Cl_4 \cdot 6CH_2Cl_2$

Selected Bond Lengths (Å)			
About Platinum			
Pt-Cl(1)	2.356 (7)	Pt-Cl(2)	2.363 (7)
Pt-P(1)	2.252 (7)	Pt-P(2)	2.278 (7)
About Phosphorus			
P(1)-C(11)	1.828 (26)	P(1)-C(21)	1.823 (19)
P(1)-C(31)	1.842 (20)	P(2)-C(15)	1.850 (20)
P(2)-C(41)	1.830 (25)	P(2)-C(51)	1.810 (22)
For Pyridine Ring			
N-C(11)	1.363 (22)	N-C(15)	1.356 (33)
C(11)-C(12)	1.359 (28)	C(12)-C(13)	1.443 (36)
C(13)-C(14)	1.367 (26)	C(14)-C(15)	1.400 (29)
C-C (av for Ph rings)	1.384 (31)		
C-Cl (av for dichloromethane)	1.781 (25)		
Selected Bond Angles (deg)			
About Platinum			
Cl(1)-Pt-Cl(2)	88.4 (2)	Cl(1)-Pt-P(1)	89.2 (2)
Cl(2)-Pt-P(1)	176.6 (2)	Cl(1)-Pt-P(2)	171.6 (2)
Cl(2)-Pt-P(2)	86.5 (2)	P(1)-Pt-P(2)	96.2 (2)
About Phosphorus			
Pt-P(1)-C(11)	109.4 (6)	Pt-P(1)-C(21)	118.9 (6)
C(11)-P(1)-C(21)	101.7 (10)	Pt-P(1)-C(31)	111.5 (6)
C(11)-P(1)-C(31)	113.5 (9)	C(21)-P(1)-C(31)	101.5 (8)
Pt-P(2)-C(15)	118.9 (6)	Pt-P(2)-C(41)	110.1 (7)
C(15)-P(2)-C(41)	99.6 (9)	Pt-P(2)-C(51)	117.1 (6)
C(15)-P(2)-C(51)	100.4 (10)	C(41)-P(2)-C(51)	109.1 (9)
About Pyridine Ring			
C(11)-N-C(15)	117.0 (17)	P(1)-C(11)-N	118.1 (15)
P(1)-C(11)-C(12)	117.9 (15)	N-C(11)-C(12)	123.1 (22)
C(11)-C(12)-C(13)	119.2 (17)	C(12)-C(13)-C(14)	118.1 (19)
C(13)-C(14)-C(15)	118.6 (22)	P(2)-C(15)-N	115.3 (14)
P(2)-C(15)-C(14)	120.9 (19)	N-C(15)-C(14)	123.7 (17)
P(1)-C(21)-C(22)	121.7 (17)	P(1)-C(21)-C(26)	120.3 (17)

with the atom-labeling scheme, is shown in Figure 3. Atomic positional parameters are given in Table II. Table III presents selected interatomic distances and angles for 6.

The platinum ions in the complex have planar geometry. The Pt-P and Pt-Cl distances are of normal lengths and are similar to those in other compounds.[16,17]

Table IV. Atom Coordinates ($\times 10^4$) and Thermal Parameters ($Å^2 \times 10^{-3}$) for $Pt_2[\mu\text{-}(Ph_2P)_2py]_2I_4 \cdot 2CH_2Cl_2$

atom	*x*	*y*	*z*	U^a
Pt	1109 (1)	1786 (1)	2810 (1)	16 (1)
I(1)	887 (1)	614 (1)	2494 (1)	27 (1)
I(2)	1467 (1)	2922 (1)	3094 (1)	25 (1)
P(1)	1185 (2)	1575 (2)	4658 (4)	18 (1)
P(2)	969 (2)	1960 (2)	955 (4)	19 (1)
N(1)	91 (5)	1619 (6)	4566 (11)	16 (5)
C(1)	508 (7)	1269 (8)	4992 (14)	20 (6)
C(2)	422 (7)	760 (7)	5641 (14)	19 (6)
C(3)	−110 (7)	615 (8)	5820 (14)	20 (6)
C(4)	−542 (7)	941 (8)	5407 (13)	20 (6)
C(5)	1318 (8)	2229 (8)	5596 (13)	25 (6)
C(6)	1878 (8)	2409 (8)	5825 (15)	27 (6)
C(7)	1998 (9)	2943 (9)	6456 (17)	42 (8)
C(8)	1573 (10)	3270 (9)	6838 (17)	44 (8)
C(9)	1027 (10)	3100 (9)	6642 (19)	48 (9)
C(10)	905 (8)	2570 (8)	5973 (14)	27 (6)
C(11)	1702 (7)	1013 (8)	5185 (14)	23 (6)
C(12)	2070 (9)	762 (10)	4472 (19)	45 (8)
C(13)	2472 (11)	333 (13)	4949 (32)	95 (15)
C(14)	2523 (13)	198 (13)	6029 (30)	99 (15)
C(15)	2170 (10)	474 (10)	6722 (22)	57 (9)
C(16)	1776 (8)	866 (9)	6281 (18)	38 (7)
C(17)	696 (7)	2731 (7)	537 (14)	18 (6)
C(18)	219 (7)	2953 (9)	979 (16)	30 (7)
C(19)	−5 (8)	3502 (9)	688 (16)	35 (7)
C(20)	237 (8)	3883 (9)	−53 (19)	43 (8)
C(21)	720 (9)	3663 (10)	−512 (18)	45 (8)
C(22)	951 (8)	3110 (8)	−176 (14)	27 (6)
C(23)	1597 (7)	1831 (7)	255 (14)	17 (6)
C(24)	2078 (7)	1661 (8)	907 (14)	25 (6)
C(25)	2568 (8)	1542 (10)	389 (16)	41 (8)
C(26)	2571 (8)	1614 (9)	−690 (15)	31 (7)
C(27)	2093 (7)	1773 (8)	−1316 (15)	26 (6)
C(28)	1613 (7)	1880 (8)	−866 (14)	23 (6)
C(29)	437 (7)	1452 (8)	220 (14)	21 (6)
Cl(1)	1152 (8)	5096 (9)	1512 (17)	
Cl(2)	1025 (9)	4721 (9)	3693 (17)	
C(30)	970 (32)	4561 (34)	2341 (64)	

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor; Cl(1), Cl(2), and C(30) were given a fixed isotropic *U* of 0.106.

The two coordination planes are well separated from one another and are required to be parallel. The nonbonded Pt⋯Pt separation is 8.2 Å. The angle between the $PtCl_2$ unit and the pyridine ring is 86°. The PpyP portions of the ring are nearly planar, as expected, with the largest deviation of any atom from the respective least-squares plane being 0.04 Å for C(14). The planes are parallel, separated by 3.01 Å, and are arranged so that the distance between the two nitrogen atoms is 3.12 Å. Each of the nitrogen lone pairs is directed into space above the other pyridine ring so that in this particular ring conformation the two nitrogen atoms do not appear to be particularly well disposed toward binding a single substrate between them.

The phosphorus atom P(1), which attaches pyridine to $PtCl_2$, completes its nearly tetrahedral coordination by two phenyl rings so that one of them (C(31)–C(36)) is nearly coplanar with the pyridine ring and is within van der Waals contact of it. The ring labeled C(21)–C(26) is normal to both the pyridine ring and the PtP_2Cl_2 plane. The P(2) atom is tetrahedrally surrounded by phenyl groups, which protrude from the central core so as to produce a globular external shape.

In the crystal the globular complex molecules form layers that are separated from one another by layers of the dichloromethane molecules. Some appreciation of this is given by the stereoscopic packing diagram shown in the supple-

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(16) Messmer, G. G.; Amma, E. L.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 725.

(17) Hitchcock, P. B.; Jacobson, B.; Pidcock, A. *J. Chem. Soc., Dalton Trans.* **1977**, 2043.

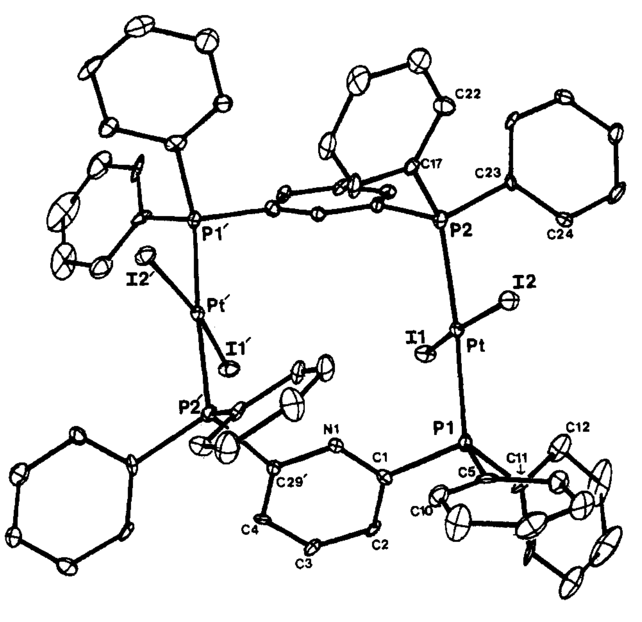


Figure 4. Perspective drawing of $Pt_2[\mu\text{-}(Ph_2P)_2py]_2I_4$ drawn using 40% thermal ellipsoids.

mentary material. The complex molecules occupy the space in the center of the unit cell while the dichloromethane molecules lie along the (100) faces of the unit cell.

The Solid-State Structure of 8, $Pt_2[\mu\text{-}(Ph_2P)_2py]_2I_4\cdot 2CH_2Cl_2$. Compound **8** is another example of a face-to-face dimer with a central 12-membered ring as shown in Figure 4. Table IV gives the atomic positional parameters. Selected interatomic distances and angles are collected in Table V. The structure of the iodo complex, **8**, differs in two significant ways from that of the chloro complex, **6**. As anticipated from the $^{31}P\{^1H\}$ NMR spectrum, *trans*-PtI_2P_2 units are present. The complex is required to have two-fold rotation symmetry.

The platinum ions are in planar environments with lengths and angles within standard ranges for this type of complex.[18] The Pt–P distances in this iodo complex are longer than they are in the chloro complex. This is a clear consequence of the trans effect, which elongates the Pt–P bond trans to phosphorus in **8** and shortens the Pt–P bond when it is trans to Cl, as in **6**. The platinum coordination planes are well separated from each other. The Pt···Pt separation is 5.33 Å, the I(1)···I(1) separation is 4.276 Å, and the I(2)···I(2) separation is 7.092 Å. The angle between the coordination planes is 28.9°. The PpyP units are planar with the largest deviation from that plane involving C(29), which is displayed by 0.036 Å. These two planes are inclined at an angle of 71.9°, and the N···N separation is 3.123 Å. A fairly open and accessible cavity exists in the center of this molecule.

The unit cell contains eight molecules of dichloromethane, which fill what would otherwise be voids in the structure. There are no unusual contacts between the dichloromethane and **8** or between two complex molecules.

Discussion

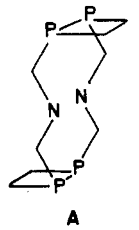
The $(Ph_2P)_2py$ ligand is capable of forming a variety of ring structures. Which of these is most stable depends on a subtle array of factors that involve at least the metal atom and the other ligands present. Solubility clearly plays a major role in determining which species can be isolated in homogeneous form. Both *cis,cis*-$Pt_2[\mu\text{-}(Ph_2P)_2py]_2Cl_4$ and *trans,trans*-$Pt_2[\mu\text{-}(Ph_2P)_2py]_2I_4$ have low solubilities under the conditions of their formation, and both spontaneously crystallize from solution.

Table V. Molecular Dimensions for $Pt_2[\mu\text{-}(Ph_2P)_2py]_2I_4\cdot 2CH_2Cl_2$

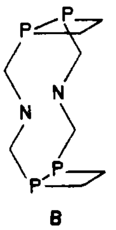
Selected Bond Lengths (A)			
About Platinum			
Pt-I(2)	2.602 (1)	Pt-I(2)	2.607 (1)
Pt-P(1)	2.307 (4)	Pt-P(2)	2.306 (5)
About Phosphorus			
P(1)-C(1)	1.840 (18)	P(1)-C(5)	1.829 (18)
P(1)-C(11)	1.816 (17)	P(2)-C(17)	1.842 (16)
P(2)-C(23)	1.829 (17)	P(2)-C(29)	1.857 (17)
In Pyridine Ring			
N(1)-C(1)	1.326 (21)	N(1)-C(29)	1.369 (22)
C(1)-C(2)	1.381 (23)	C(2)-C(3)	1.356 (24)
C(3)-C(4)	1.320 (23)	C(4)-C(29)	1.381 (24)
C-C (av for Ph rings)	1.374 (32)		
C-Cl (av for dichloromethane)	1.656 (82)		
Selected Bond Angles (deg)			
About Platinum			
I(1)-Pt-I(2)	172.5 (1)	I(1)-Pt-P(1)	87.3 (1)
I(2)-Pt-P(2)	93.2 (1)	I(1)-Pt-P(2)	90.0 (1)
I(2)-Pt-P(2)	89.8 (1)	P(1)-Pt-P(2)	175.6 (2)
About Phosphorus			
Pt-P(1)-C(1)	107.2 (6)	Pt-P(1)-C(5)	117.6 (6)
C(1)-P(1)-C(5)	104.2 (8)	Pt-P(1)-C(11)	118.3 (6)
C(1)-P(1)-C(11)	106.0 (8)	C(5)-P(1)-C(11)	102.2 (8)
Pt-P(2)-C(17)	116.1 (6)	Pt-P(2)-C(23)	112.6 (5)
C(17)-P(2)-C(23)	107.3 (8)	Pt-P(2)-C(29)	114.8 (6)
C(17)-P(2)-C(29)	100.5 (7)	C(23)-P(2)-C(29)	104.3 (8)
In Pyridine Ring			
C(1)-N(1)-C(29)	117.3 (14)	P(1)-C(1)-N(1)	111.3 (12)
P(1)-C(1)-C(2)	126.4 (13)	N(1)-C(1)-C(2)	122.2 (16)
C(1)-C(2)-C(3)	117.9 (15)	C(2)-C(3)-C(4)	122.7 (16)
C(3)-C(4)-C(29)	117.5 (16)	P(1)-C(5)-C(6)	116.7 (13)

The *trans,trans*-$Pt_2[\mu\text{-}(Ph_2P)_2py]_2I_4$ structure is characteristic of a number of large-ring metal complexes. On the other hand, the *cis,cis*-$Pt_2[\mu\text{-}(Ph_2P)_2py]_2Cl_4$ structure is unusual, although a related structure has been observed for $Pt_2(\mu\text{-}Ph_2PCH_2PPh_2)_2(CH_3)_4$.[19] In this case the large trans effect of the methyl groups must be responsible for directing the orientation of the ligands so that the methyl groups avoid positions that are mutually trans.

For the 12-membered ring in $Pt_2[\mu\text{-}(Ph_2P)_2py]_2Cl_4$ molecular models indicate that there are two cis,cis conformations, A and B, which can exist and that these cannot be interconverted without bond rupture. The substance that we have



A



B

examined by X-ray diffraction has conformation A. The other isolated molecule, **7**, whose ^{31}P NMR spectrum appears in trace C of Figure 2, could be the isomeric substance with structure B, but it could as well have a different ring size (degree of polymerization). The available data do not allow us to discriminate between these possibilities.

The ^{31}P NMR studies have revealed some aspects of the formation of these large-ring compounds. With both palladium(II) and platinum(II), the phosphine ligand is rapidly (within 5 min) bound to metal ions; with the palladium(II) chloride complex **3**, the thermodynamically stable polymer is

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[18] Hitchcock, P. B.; Jacobson, B.; Pidcock, A. *J. Chem. Soc., Dalton Trans.* **1977**, 2038.

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Table VI. Crystal Data

	$[C_{29}H_{23}NP_2]_2Pt_2Cl_4 \cdot 6CH_2Cl_2$ (6)	$[C_{29}H_{23}NP_2]_2Pt_2I_4 \cdot 2CH_2Cl_2$ (8)
fw (dimer + solvent)	1936.5	1962.6
mp, °C	>250	>250
cryst dimens, mm	0.05 × 0.35 × 0.25	0.11 × 0.02 × 0.014
color	colorless	orange
unit cell dimens (140 K)		
a, Å	16.17 (4)	24.093 (7)
b, Å	14.60 (4)	21.544 (6)
c, Å	16.36 (6)	12.287 (3)
β, deg	110.9 (2)	95.08 (2)
V, Å^3	3608	6352
space group	$P2_1/c$	$C2/c$
D_{exptl}, Mg m^{-3} (20 °C)	1.9	2.0
D_{calcd}, Mg m^{-3} (140 K)	1.8	2.05
F(000)	1888	3680
Z	2	4
radiatn, λ, Å (graphite monochromator)	Mo, 0.710 69	Mo, 0.710 69
μ(Mo Kα), cm^{-1}	41.8	66.8
scan type (2θ max, deg)	ω (45)	ω (45)
scan range, deg	1.3	1.0
bkgd offset, deg	see text	±1.0
bkgd scan time, s	see text	1.0
scan speed, deg min^{-1}	8	58.6
check reflcns; interval no.	(2,0,−4), (2,4,−4); 198	(4,8,−2), (6,0,4); 198
no. of unique ($F > 6\sigma(F)$)	3005	3102
R	0.066	0.056
R_w	0.065	0.058
no. of parameters	465	325

formed in high yield. With platinum, however, a variety of materials is formed. These are apparently various polymers that then slowly rearrange to give, in the two cases studied, products of low solubility that precipitate from solution. In the process the Pt–P bonds must break and re-form to give the final product.

Experimental Section

Preparation of Compounds. $(Ph_2P)_2py$ was prepared as previously reported.[20] The complexes reported here are not sensitive to atmospheric oxygen or moisture, and no special precautions are necessary to protect them from air.

$Pd_3[\mu\text{-}(Ph_2P)_2py]_3Cl_6$. $(COD)PdCl_2$ (0.934 g, 3.25 mmol) was dissolved in a dichloromethane solution (20 mL) containing $(Ph_2P)_2py$ (1.45 g, 3.24 mmol). The solution slowly changed color from yellow to light orange wth the concurrent production of the strong odor of 1,5-cyclooctadiene. After 30 min the solution was concentrated by rotary evaporation and diethyl ether was added to precipitate the product. The crystals (1.66 g, 82%) were removed by filtration and recrystallized from dichloromethane/ether. Anal. Calcd for $C_{29}H_{23}NP_2Cl_2Pd$: C, 55.71; H, 3.72; N, 2.24; Cl, 11.35. Found: C, 55.03; H, 3.93; N, 2.20; Cl, 11.02.

$Pt_2[\mu\text{-}(Ph_2P)_2py]_2Cl_4$. The ligand $(Ph_2P)_2py$ (0.234 g, 0.523 mmol) was dissolved in dichloromethane (10 mL) and added to a dichlormethane solution (30 mL) containing $(COD)PtCl_2$ (0.197 g, 0.524 mmol). The reaction mixture sat overnight at room temperature. The colorless crystals that had deposited (0.279 g, 75%) were filtered, washed with dichloromethane, and vacuum-dried. The vacuum drying removes the lattice-trapped dichloromethane seen in the X-ray diffraction study and results in fragmentation of the crystals. Anal. Calcd for $C_{29}H_{23}NP_2Cl_2Pt$: C, 48.82; H, 3.26; N, 1.96. Found: C, 48.37; H, 3.34; N, 1.93.

$Pt_2[\mu\text{-}(Ph_2P)_2py]_2I_4$. The ligand $(Ph_2P)_2py$ (0.165 g, 0.369 mmol) was dissolved in benzene (20 mL) and added to benzene solution (40 mL) containing $(COD)PtI_2$ (0.207 g, 0.370 mmol). There was an immediate color change from yellow to dark orange. The solution was heated under reflux for 2 h and concentrated by rotary evaporation. Slow evaporation of the resulting solution yielded orange crystals, of excellent quality, of the desired product (0.139 g, 42%).

NMR Measurements. All $^{31}P\{^1H\}$ NMR spectra were recorded at 81.0 MHz with a Nicolet NT-200 spectrometer, operated with quadrature detection. The ^{31}P spectra were all obtained with use of 12-mm tubes, broad-band proton decoupling, and an external 85% phosphoric acid reference. The spectra were taken with a 7-μs pulse length (40°) and with 800-ms repetition rates. The high-frequency-positive convention, recommended by IUPAC, is used in reporting chemical shifts.

X-ray Data. All data were collected on a Syntex $P2_1$ diffractometer equipped with a locally modified LT-1 low-temperature device. The high-speed data collection technique used for **8** has been described elsewhere.[21a]

Colorless crystals of $Pt_2[\mu\text{-}(Ph_2P)_2py]_2Cl_4 \cdot 6CH_2Cl_2$ (**6**) were obtained by slow diffusion of diethyl ether into a dichloromethane solution of the complex. The crystals were well-formed, thin plates with the form (100) developed. However, any slight touch caused the plates to split into thin sheets, with serious misalignment about the direction normal to the plates. All crystals examined were therefore of poor crystallographic quality; typical ω scans were 4° or wider. The mechanical properties of the crystals correlate very well with the structure. Layers of dichloromethane are present between the platinum dimers, in planes parallel to 100 (vide supra). The crystal finally selected for intensity measurements was carefully picked from the solution with a glass mounting fiber and immediately placed in the cold stream of the low-temperature apparatus. Because of the wide ω scan range it was impossible to scan the entire peak without picking up intensity from neighboring reflections, and separate backgrounds could not be measured. Intensities were measured with 1.3° ω scans; backgrounds were estimated from a background curve obtained from areas with no discernible peaks. Other details of the data collection are in Table VI.

Orange crystals of $Pt_2[\mu\text{-}(Ph_2P)_2py]_2I_4 \cdot 2CH_2Cl_2$ (**8**) were formed by slow vapor diffusion of diethyl ether into a dichloromethane solution of the compound. Details of the data collection are given in Table VI.

Solution and Refinement of the Structures. All calculations were done on a Data General ECLIPSE computer. Except for the absorption corrections and background and Lp correction for **6** we used the SHELXTL system. The form factors, including anomalous scattering, were from ref 21b.

Both structures were solved by Patterson and heavy-atom methods and initially refined with isotropic temperature factors. For **8** the correct choice of space groups as $C2/c$ (rather than Cc) was verified by satisfactory refinement using that space group. After convergence ($R = 0.15$ for **6**, 0.09 for **8**) an empirical absorption correction[22] was

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(20) Newkome, G. R.; Hager, D. C. *J. Org. Chem.* **1978**, *43*, 947.

(21) (a) Hope, H.; Nichols, B. E. *Acta Crystallogr. Sect. B: Struct. Crystallogr. Cryst. Chem.* **1981**, *B37*, 158. (b) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

Inorg. Chem. **1984**, *23*, 4315–4321

applied. Especially for **6** this resulted in a dramatic data improvement. The program is designed so that it will attempt to correct for systematic intensity errors such as those caused by the partial ω scans described above. The *R* index dropped to 0.07, and most of the H atoms could be located in a difference map. In the final stages of the refinement all non-hydrogen atoms were given anisotropic temperature factors. The hydrogen atoms were included as fixed-group atoms with thermal parameters linked to the anchor atoms. Refinement was by the block-cascade technique of the SHELXTL system.

Acknowledgment. We thank the National Science Foundation (Grant CHE 8217954) for financial support. J.H. is grateful for sabbatical leave support from the Norwegian Research Council for the Sciences and Humanities. F.E.W. was a University of California Regents Fellow.

Registry No. **3**, 87039-36-9; **2**, 93000-14-7; **7**, 92958-57-1; **8**, 92958-59-3; Pd[$(Ph_2P)_2$py]Cl_2, 92984-18-4; Pd_3[μ-$(Ph_2P)_2$py]$_3Br_6$, 92958-60-6; [Pd($(Ph_2P)_2$py)Br_2]$_n$, 92958-62-8; (COD)$PdCl_2$, 12107-56-1; (COD)$PtCl_2$, 12080-32-9.

Supplementary Material Available: Tables of structure factors, atomic thermal parameters, hydrogen atom positions, and bond angles and bond lengths for both *cis,cis*-Pt_2[μ-$(Ph_2P)_2$py]$_2Cl_4\cdot 6CH_2Cl_2$ and *trans,trans*-Pt_2[μ-$(Ph_2P)_2$py]$_2I_4\cdot 2CH_2Cl_2$ and a packing diagram for the former compound (46 pages). Ordering information is given on any current masthead page.

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[22] The method obtains an empirical absorption tensor from an expression F_o and F_c: Hope, H.; Moezzi, B. Department of Chemistry, University of California, Davis, CA.

Contribution from Anorganische Chemie III, Eduard-Zintl-Institut
der Technischen Hochschule Darmstadt, D-6100 Darmstadt, Federal Republic of Germany

Ligand Substitution in Molybdenum(0) Carbonyl Complexes $Mo(CO)_5$(amine) and *cis*-$Mo(CO)_4$(amine)$_2$: Kinetics and High-Pressure Effects

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Received December 15, 1983

Visible spectrophotometry at ambient and at high pressure has been applied to study the kinetics of ligand substitution in molybdenum(0) carbonyl complexes *cis*-$Mo(CO)_4(py)_2$ (py = pyridine) and $Mo(CO)_5$(amine) (amine = py, 4-Mepy (4-methylpyridine), 4-CNpy (4-cyanopyridine)) by bidentate nitrogen donor ligands $N^\frown N$ (= dab (biacetyl bis(phenylimine)), dab-OCH_3 (biacetyl bis((4-methoxyphenyl)imine)), dab-Cl (biacetyl bis((4-chlorophenyl)imine)), bpy (2,2′-bipyridine), phen (1,10-phenanthroline)) in the solvent toluene to form $Mo(CO)_4(N^\frown N)$. The rate of product formation follows the one-term rate law rate = k_{obsd}[*cis*-$Mo(CO)_4(py)_2$] and rate = k_{obsd}[$Mo(CO)_5$(amine)], respectively. It has been found for system A (*cis*-$Mo(CO)_4(py)_2/N^\frown N$/toluene) and for system B ($Mo(CO)_5$(amine)/$N^\frown N$/toluene) that rate constant k_{obsd} is independent of both the concentration and the nature of the incoming chelate ligand $N^\frown N$. For system A the rate-reducing effect of excess pyridine added to the system can be quantitatively accounted for by mass law retardation, which strongly supports system A to follow a pure D mechanism. The activation parameters found for system A are $\Delta H^* = 24.5$ kcal·mol^{-1}, $\Delta S^* = 13.5$ eu, and $\Delta V^* = 3.6$ cm^3·mol^{-1} ($N^\frown N$ = dab). For system B (with amine = 4-Mepy) the rate of substitution at 25 °C is approximately 120 times smaller than for system A and rate constant k_{obsd} depends on the basicity of the leaving amine ligand. The nature of the rate-reducing effect of excess pyridine added to system B (with amine = py) is more complex than in system A. The activation parameters obtained for system B (with amine = 4-Mepy) are $\Delta H^* = 23.3$ kcal·mol^{-1}, $\Delta S^* \approx 0$, and $\Delta V^* \approx 0$. Most of the kinetic data collected for system B support a dissociatively controlled mechanism.

Introduction

The activation volume ΔV^* as obtained from high-pressure studies has become a well-established tool for the investigation of the mechanism of substitution reactions in transition-metal complexes.[1] Despite an increasing interest in the mechanistic pathways for ligand substitution processes in transition-metal carbonyls[2] the information available on the effect of pressure on the reaction of carbonyls is very scarce. Brower and Chen[3] reported in 1973 first-order kinetics and positive ΔV^* values for monodentate nucleophiles entering $Ni(CO)_4$, $Mo(CO)_6$, and $Cr(CO)_6$. For the analogous reaction of $W(CO)_6$, which is described to be of second order, a negative activation volume was obtained. No information appears to be available on the effects of high pressure on the substitution kinetics in octahedral carbonyl complexes of the type $M(CO)_5L$ and $M(CO)_4L_2$.

The present work was undertaken to study the kinetics of two types of substitution reactions that are known to be of considerable preparative importance (eq 1 and 2; $N^\frown N$ = bidentate nitrogen donor). This contribution presents rate

$$cis\text{-}M(CO)_4(\text{amine})_2 + N^\frown N \rightleftharpoons M(CO)_4(N^\frown N) + 2\,\text{amine} \quad (1)$$

$$M(CO)_5(\text{amine}) + N^\frown N \rightleftharpoons M(CO)_4(N^\frown N) + \text{amine} + CO \quad (2)$$

constants, rate laws, and activation parameters (including ΔV^*) for reactions 1 and 2 as studied for M = Mo(0) and amine = py (pyridine or pyridine substituted in the 4-position) in toluene as solvent. The bidentate nitrogen donor $N^\frown N$ represents chelate ligands such as bpy (2,2′-bipyridine), phen (1,10-phenanthroline), and dab (biacetyl bis(phenylimine)).

Experimental Section

Ligands and Complexes. The ligands bpy, phen·H_2O, py, 4-Mepy (γ-picoline), and 4-CNpy (4-cyanopyridine) were analytical grade. The ligand dab and the corresponding substituted ligands dab-Cl (biacetyl bis((4-chlorophenyl)imine)) and dab-OCH_3 (biacetyl bis((4-methoxyphenyl)imine)) were prepared by condensation of 1 mol of biacetyl with 2 mol of aniline (dab), 4-chloroaniline (dab-Cl), or 4-methoxyaniline (dab-OCH_3) in *i*-PrOH and recrystallization from

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