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Solvent-Controlled Equilibria of Substitution and Isomerization of α-Ketoacyl Complexes of Platinum(II). X-ray Single-Crystal Structure of *cis*-Pt(COCOPh)(Cl)($PPh_2CH_2CH_2PPh_2$)

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The reactions of *trans*-Pt(COCOR)(Cl)(PPh_3)$_2$ (R = Ph (**1**), OMe (**2**)) with dppe ((diphenylphosphino)ethane) or dppp ((diphenylphosphino)propane) in $CHCl_3$ led to the formation of the ionic complexes *cis*-[Pt(COCOR)(PPh_3)(dppe)](Cl) (R = Ph (**3**), OMe (**4**)). The substitution reactions are reversible. Attempts for the isolation of **3** and **4**, respectively, resulted in the neutral products *cis*-Pt(COCOR)(Cl)(dppe) (R = Ph (**6**), OMe (**7**)), which could also be independently formed by the analogous substitution reactions in benzene. Reactions of complexes **6** and **7** with PPh_3 in $CHCl_3$ gave ionic **3** and **4**, respectively, but in benzene afforded neutral complexes **1** and **2** instead. The dynamic equilibrium between **3** and **6** could be simply controlled by varying the solvents. Such bidentate ligand-induced, solvent-controlled, reversible processes of substitution and isomerization appear to be general to the square-planar organoplatinum(II) and organopalladium(II) complexes with the general formula *trans*-M(R)(X)L_2. The single-crystal structure of complex **6** has been determined by X-ray diffraction, with crystal data $P2_12_12_1$, a = 10.620 (2) Å, b = 12.151 (5) Å, c = 23.920 (6) Å, V = 3087 (2) Å^3, Z = 4, μ = 48.1 mm^{-1}, T = 300 K, total reflections 3073, observed reflections 2283 ($I > 2.0\sigma(I)$), R = 0.048, and R_w = 0.033. The two vicinal carbonyls of such a cis α-ketoacyl complex of platinum(II) are noncoplanar, having a torsional angle of 127 (1)°.

Introduction

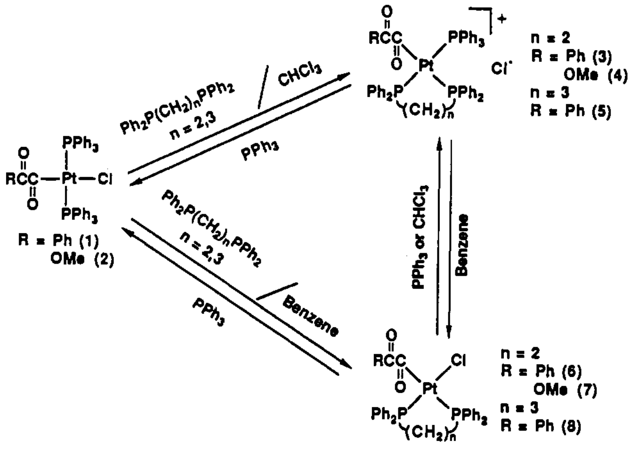
It has been known for a long time that d^8 square-planar monoorganometals with the formula $MRXL_2$ (wherein X = halide and L = tertiary phosphine) prefer trans geometry.[1] The cis isomers of alkyl or aryl derivatives can be readily prepared by the displacement of halide in *cis*-MX_2L_2, by using equimolar amounts of appropriate Grignard reagent or organolithium (eq 1), but not

$$cis\text{-}MX_2L_2 + RMgX\ (\text{or } RLi) \rightarrow cis\text{-}MRXL_2 + MgX_2\ (\text{or } LiX) \qquad (1)$$

$$trans\text{-}MRXL_2 + L'\text{-}L' \rightarrow cis\text{-}MRX(L'\text{-}L') + 2L \qquad (2)$$

by the oxidative-addition reactions. Lack of the convenient nucleophilic acyl reagents makes the synthesis of the cis acyl complexes by the methods of eq 1 difficult.[2] An intuitively feasible synthetic route for cis square-planar monoorganometal complexes is via the substitution-isomerization reactions of $MRXL_2$ with a bidentate ligand L′-L′, as shown in eq 2. Analogous reactions of eq 2 for the inorganic complexes MX_2L_2 are well documented.[3] Therefore, reactions for the organometallic compounds are probably taken for granted, so that systematic investigations of them are often neglected. Such seemingly straightforward reactions are actually more complicated than simple displacement of ligands. A wide product distribution from the expected mononuclear *cis*-MRX(L′-L′) to the unexpected "A-frame" complexes, as well as many inorganic byproducts, varying with the bidentate, organic, and halide ligands, have been reported.[4] Reactions of eq 2 for the acyl derivatives still are among the category of the little studied.[5]

Scheme I



During our attempts of preparing the cis α-ketoacyl complexes, using the bidentate phosphino ligands, it has been found that distinct products in either the ionic or the neutral form were obtained in different solvents. The isomerizations of the stable *cis*-$MRXL_2$ to the trans form are known to be induced by the free ligand L in solutions.[1a] Such reactions appear similar to the well-known cis–trans isomerization of the inorganic complexes MX_2L_2.[6] Mechanistic studies on some platinum(II) and palladium(II) systems have afforded the evidence that the isomerizations of the complexes ligated with convenient ionic leaving groups (such as halides) could be facilitated by undergoing transformation to ionic intermediates $[MXL_3]^+X^-$, particularly, in polar solvents (eq 3).[7] An alternative mechanism involving

$$cis\text{-}MX_2L_2 \rightarrow [MXL_3]^+X^- \rightarrow trans\text{-}MX_2L_2 \qquad (3)$$

$$cis\text{-}MX_2L_2 \rightarrow [MX_2L_3] \rightarrow trans\text{-}MX_2L_2 \qquad (4)$$

the pseudorotation of five-coordinate intermediates as in eq 4 has also been proposed.[8] However, distinguishable and well-characterized examples of eqs 3 and 4 for the d^8 organometal complexes are rare,[9] presumably due to the paucity of *cis*-$MRXL_2$. In this paper, we would like to report the solvent-controlled

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Table I. Selected Spectroscopic Data

compd	λ_{max}, nm (ϵ, M^{-1} cm^{-1})[a]	ν_{CO}, cm^{-1}	NMR[a] δ(^{31}P) (*J*, Hz)	NMR[a] δ(^1H) (*J*, Hz)
cis-[Pt(COCOPh)(PPh_3)(dppe)](Cl) (**3**)	504 (95 ± 1)	1659, 1648[a]	40.56 (2810, 306.4, 10.0), 36.10 (1573, 22.6, 10.0), 16.04 (2979, 306.4, 22.6)	
cis-[Pt(COCOPh)(PPh_3)(dppe)](BF_4) (**3a**)		1659, 1648[a]	40.56 (2810, 306.4, 10.0), 36.10 (1573, 22.6, 10.0), 16.04 (2979, 306.4, 22.6)	
cis-[Pt(COCOOMe)(PPh_3)(dppe)](Cl) (**4**)		1730 (sh), 1704, 1659[a]	41.30 (2725, 303.2, 9.7), 36.79 (1610, 22.2, 9.7), 15.72 (2922, 303.2, 22.2)	3.05 (s, OCH_3)
cis-[Pt(COCOPh)(PPh_3)(dppp)](Cl) (**5**)		1665, 1650[a]	16.44 (2998, 305.4, 31.5), −10.25 (2774, 36.6, 31.5), −9.67 (1508, 305.4, 36.6)	
cis-Pt(COCOPh)(Cl)(dppe) (**6**)	456 (380 ± 10)	1664, 1621, 1642 (sh)[c]	35.15 (4257, 4.1), 33.22 (1568, 4.1)	
cis-Pt(COCOOMe)(Cl)(dppe) (**7**)		1720, 1636[c]	34.65 (1650, 5.8), 34.40 (4145, 5.8)	3.55 (s, OCH_3)
cis-Pt(COCOPh)(Cl)(dppp) (**8**)		1659, 1624, 1643 (sh)[b]	−3.96 (4219, 28.7), −5.24 (1473, 28.7)[b]	
cis-[Pd(COCOPh)(PPh_3)(dppe)](Cl) (**10**)		1677, 1636[a]	44.2 (21.4), 31.7 (21.4)	
cis-Pd(COCOPh)(Cl)(dppe) (**11**)		1675, 1636[b]	44.27 (43.5), 25.17 (43.5)[b]	
cis-[Pt(COPh)(PPh_3)(dppe)](Cl) (**13**)		1610[a]	38.08, (3179, 311.4, 6.8), 37.12 (1419, 22.3, 6.8), 17.03 (3051, 311.4, 22.3)	
cis-Pt(COPh)(Cl)(dppe) (**14**)		1632[b]	29.92 (4266, 3.4), 33.25 (1448, 3.4)[b]	
cis-[Pt(Me)(PPh_3)(dppe)](I) (**16**)			53.50 (2743, 381.4, 5.3), 49.95 (1807, 16.7, 5.3), 26.49 (2769, 381.4, 16.7)	0.42 (m, CH_3, J_{Pt-H} = 57.0)
cis-Pt(Me)(I)(dppe) (**17**)			45.00 (3918), 44.39 (1706)[b]	0.58 (m, CH_3, J_{Pt-H} = 75.0)[b]
cis-$PtCl_2$(dppe) (**18**)			41.53 (3620)	
[Pt$(dppe)_2$]Cl_2 (**19**)			47.73 (2362)	

[a] Measured in chloroform. [b] Measured in benzene. [c] Measured as KBr pellets.

Table II. X-ray Crystal Parameters and Data Collection for Complex **6**

formula	$C_{34}H_{29}O_2ClP_2Pt$	radiation λ, Å	0.7107
fw	762.10	*T*, K	300
cryst dimens, mm	0.3 × 0.4 × 0.4	μ, mm^{-1}	48.1
space group	$P2_12_12_1$	transm	0.820–0.999
a, Å	10.620 (2)	2θ, deg	50
b, Å	12.151 (5)	*h*,*k*,*l*	12,14,28
c, Å	23.920 (6)	no. of reflns measd	3073
α, deg	90	no. of reflns obsd	2283 (>2.0σ)
β, deg	90	no. of variables	361
γ, deg	90	*R*(*F*)	0.048
V, $Å^3$	3087 (2)	$R_w(F)$	0.033
Z	4	*S*	2.55
ρ(calcd), g·cm^{-3}	1.58	$(\Delta/\sigma)_{max}$	0.38
F(000)	1496		

Table III. Non-Hydrogen Atomic Coordinates for Complex **6**

	x	*y*	*z*	B_{iso},[a] $Å^2$
Pt	0.71384 (6)	0.53375 (5)	0.10228 (3)	4.15 (3)
Cl	0.9347 (3)	0.5374 (4)	0.08718 (18)	7.5 (3)
P1	0.6618 (4)	0.6602 (4)	0.03421 (18)	5.28 (24)
P2	0.5129 (4)	0.5288 (4)	0.12135 (17)	5.48 (24)
C1	0.4894 (15)	0.6603 (15)	0.0322 (6)	6.8 (11)
C2	0.4376 (14)	0.6458 (14)	0.0896 (7)	7.6 (11)
C3	0.7718 (19)	0.4270 (12)	0.1684 (6)	8.7 (12)
O3	0.7457 (11)	0.4534 (11)	0.2173 (4)	10.1 (9)
C4	0.8300 (18)	0.3288 (13)	0.1583 (8)	9.5 (13)
O4	0.7733 (15)	0.2700 (9)	0.1222 (5)	12.8 (10)
C11A	0.7092 (15)	0.7986 (12)	0.0537 (5)	5.5 (9)
C12A	0.7909 (16)	0.8175 (11)	0.0901 (6)	6.1 (9)
C13A	0.8313 (16)	0.9256 (12)	0.1032 (7)	8.5 (12)
C14A	0.7863 (17)	1.0108 (12)	0.0766 (6)	8.1 (11)
C15A	0.6970 (17)	0.9935 (12)	0.0384 (6)	8.7 (11)
C16A	0.6591 (17)	0.8856 (15)	0.0244 (7)	8.9 (12)
C11B	0.7072 (16)	0.6371 (12)	−0.0371 (6)	6.0 (9)
C12B	0.6496 (16)	0.6942 (15)	−0.0850 (7)	10.0 (13)
C13B	0.6761 (18)	0.6728 (17)	−0.1394 (6)	10.4 (14)
C14B	0.7696 (19)	0.6014 (14)	−0.1495 (6)	9.1 (12)
C15B	0.8314 (17)	0.5533 (14)	−0.1066 (8)	11.3 (14)
C16B	0.8024 (19)	0.5702 (14)	−0.0495 (6)	10.1 (13)
C21A	0.4307 (15)	0.4129 (13)	0.0924 (8)	7.8 (11)
C22A	0.4858 (16)	0.3361 (15)	0.0653 (8)	9.3 (13)
C23A	0.4260 (21)	0.2503 (18)	0.0357 (10)	13.4 (19)
C24A	0.2983 (21)	0.2385 (14)	0.0505 (9)	11.7 (15)
C25A	0.2259 (19)	0.3131 (16)	0.0821 (9)	14.1 (17)
C26A	0.2966 (16)	0.4028 (13)	0.1059 (8)	9.3 (12)
C21B	0.4712 (15)	0.5569 (13)	0.1941 (7)	7.4 (11)
C22B	0.4312 (18)	0.4748 (20)	0.2238 (7)	11.8 (16)
C23B	0.4067 (19)	0.4722 (25)	0.2885 (8)	16.3 (20)
C24B	0.4173 (23)	0.5830 (22)	0.2996 (10)	16.0 (21)
C25B	0.468 (3)	0.6693 (23)	0.2773 (10)	21.4 (27)
C26B	0.4898 (22)	0.6506 (21)	0.2193 (8)	13.4 (18)
C41	0.9480 (18)	0.2830 (15)	0.1855 (8)	9.0 (13)
C42	0.973 (3)	0.1718 (19)	0.1827 (13)	23.0 (27)
C43	1.069 (3)	0.1422 (21)	0.2125 (12)	21.4 (25)
C44	1.1338 (21)	0.2163 (19)	0.2396 (8)	14.1 (18)
C45	1.1162 (17)	0.3258 (21)	0.2429 (8)	11.3 (16)
C46	1.0084 (17)	0.3666 (16)	0.2153 (7)	8.3 (13)

[a] $B_{iso} = (8\pi^2/3)\sum_i\sum_j u_{ij}a_i^*a_j^*a_ia_j$.

substitution and isomerization reactions of the rare (α-ketoacyl)platinum(II) complexes and their dynamic equilibria. The generalization of such reactivity to other organoplatinum and organopalladium systems might serve as a guideline for the solvent effect in many platinum- and palladium-catalyzed chemical processes.

Results

The transformations observed in this work are summarized in Scheme I. Reactivity studies were undertaken, whose spectroscopic data are presented in Table I. A structure study was undertaken for complex **6**, whose results are presented in Tables II–IV. These will be introduced at appropriate places in the sections that follow.

Discussion

Reactions of *trans*-Pt(COCOR)(Cl)$(PPh_3)_2$ with dppe in Chloroform. Reactions of *trans*-Pt(COCOR)(Cl)$(PPh_3)_2$ (R = Ph (**1**), OMe (**2**)) with equimolar amounts of dppe in $CHCl_3$ led to the instantaneous displacement of the chloride ion and a PPh_3 to form ionic *cis*-[Pt(COCOR)(PPh_3)(dppe)](Cl) (R = Ph (**3**), OMe (**4**)) in over 90% conversion. There was a minute amount of starting materials left unreacted. Analogous reaction of **1** with dppp ((diphenylphosphino)propane) proceeded in a similar manner to yield *cis*-[Pt(COCOR)(PPh_3)(dppp)](Cl) (**5**). The rosy $CHCl_3$ solution of **3** exhibited a UV–vis electronic band at 504 nm with ϵ_{max} = 95 ± 1 M^{-1} cm^{-1}. Excess dppe or longer reaction time would result in the production of $PtCl_2$(dppe) (**18**) and [Pt$(dppe)_2$]Cl_2 (**19**).[10,11]

Table IV. Selected Bond Distances (Å) and Angles (deg) for *cis*-[Pt(COCOPh)(Cl)(dppe) (6)

Pt–Cl	2.373 (4)	Pt–C3	2.14 (2)	Pt–P1	2.306 (4)
Pt–P2	2.183 (4)	C1–C2	1.49 (2)	C3–O3	1.24 (2)
C3–C4	1.37 (2)	C4–O4	1.27 (2)	C4–C41	1.52 (3)
Cl–Pt–P1	96.7 (2)	Pt–C3–O3	118.4 (12)	Cl–Pt–P2	176.7 (2)
Pt–C3–C4	122.0 (12)	Cl–Pt–C3	80.8 (5)	O3–C3–C4	119.5 (15)
P1–Pt–P2	86.1 (2)	C3–C4–O4	113.4 (17)	P1–Pt–C3	175.2 (5)
C3–C4–C41	128.3 (17)	P2–Pt–C3	96.3 (5)	O4–C4–C41	118.3 (15)

The infrared absorptions of the α-ketoacyl carbonyls in **3** were observed at 1659 and 1648 cm^{-1} and at 1730 (sh), 1704, and 1659 cm^{-1} for **4**, respectively. The ^{31}P NMR spectrum of **3** comprises three sets of doublets of doublets at δ 40.56 (J = 306.4, 10.0 Hz), 36.10 (J = 22.6, 10.0 Hz), and 16.04 (J = 306.4, 22.6 Hz) with their distinguishable P–Pt coupling constants being 2810, 1573, and 2979 Hz, respectively. The first two resonances are assigned to the phosphorus nuclei of dppe. Of them, the one trans to the α-ketoacyl ligand is of the smallest $J_{\text{P-Pt}}$ value. And, the high-field peaks are ascribed to PPh$_3$. The ^{31}P NMR spectra of **4** and **5** have similar features where data and other selected spectroscopic data are listed in Table I. These spectra suggest that complexes **3**, **4**, and **5** are likely in cis square-planar structures.

In acetonitrile, a 1.1 × 10^{-3} M solution of **3** exhibited an equivalent conductance of 94 cm^2 eq^{-1} Ω^{-1}, which was substantially larger than that of the neutral complex **1**, being only 2.9 cm^2 eq^{-1} Ω^{-1}. This experiment strongly supports the ionic character of **3**. Treatment of **3** with 1 equiv of AgBF$_4$ immediately caused the white precipitation of AgCl. But, the product of main interest *cis*-[Pt(COCOR)(PPh$_3$)(dppe)](BF$_4$) (**3a**) is too hygroscopic to be isolated as solid. Attempts for the isolation of **3** and **4** by recrystallization from CHCl$_3$/Et$_2$O cosolvents resulted in the recovery of neutral products, *cis*-Pt(COCOR)(Cl)(dppe) (R = Ph (**6**), OMe (**7**)) (vide supra).

Reactions of *trans*-Pt(COCOR)(Cl)(PPh$_3$)$_2$ with dppe in Benzene. Complexes **6** and **7** could also be obtained in a better yield (>95%) by the reactions of **1** and **2** with dppe in benzene, respectively. Analogous reaction of **1** and dppp afforded *cis*-Pt(COCOR)(Cl)(dppp) (**8**) in a comparable yield. When the neutral products were in solution in the presence of the replaced PPh$_3$, broadened phosphorus resonances, presumably due to the phosphine exchange between free PPh$_3$ and the coordinated bidentates, were observed in their ^{31}P NMR spectra. In contrast, the isolated samples show well-resolved peaks in an AB pattern with distinct $J_{\text{P-Pt}}$ values, which fit a cis square-planar geometry. As listed in Table I, the P–Pt couplings for the phosphorus nucleus trans to an α-ketoacyl ligand are around 1500 Hz and are slightly larger than the values of $J_{\text{Pt-P}}$ corresponding to the acyl analogues. It suggests that the α-ketoacyl ligand may be a weaker donor than the acyl analogue. Meanwhile, the phosphorus nuclei that are trans to the chloride show their P–Pt couplings at over 4000 Hz, which is normal.

X-ray Structure of *cis*-Pt(COCOPh)(Cl)(PPh$_3$)$_2$. The X-ray diffraction study for complex **6** has confirmed its distorted square-planar molecular structure. This is the first *cis*-(α-ketoacyl)platinum(II) complex that has been crystallographically characterized. Its crystal data, atomic coordinates, and selected bond distances and bond angles are listed in Tables II–IV, respectively. Figure 1 displays its ORTEP drawing. One may notice that the ratio of the number of measured reflections to the number of variables ≈6 is slightly low. And, the thermal parameters of a few carbon atoms in the α-ketoacyl phenyl group appear to be large. The ∠Cl–Pt–C3 shows severe distortion to 80.8 (5)°. The two Pt–P bonds have different bond lengths. The bond distance of Pt–P2, 2.183 (4) Å, is shorter than the average Pt–P bond distance (2.3 Å)[2a,11c] and, specifically, is shorter than a bond involving a phosphorus trans to a chloride ligand, such as that in Pt(dppe)Cl$_2$ (2.23 Å).[11b] The Pt–C3 bond (2.14 (2) Å) is found to be longer than the 1.98 Å suggested for a typical Pt–C(sp^2) bond,[2a] and the C3–C4 bond, 1.37 (2) Å, is relatively short in comparison with those of other (α-ketoacyl)platinum complexes (1.54–1.59 Å),[12] in spite of the thermal uncertainty that limits the exact comparison. The most intriguing structural feature in **6**, which is noticeably distinct from that of other known trans α-ketoacyl complexes of platinum(II), is the noncoplanarity of the oxalyl (–COCO–) group. The torsional angle O3–C3–C4–O4 = 127 (1)° is substantially smaller than those of all known α-ketoacyl complexes (157–177°),[12] except a cyclopentadienylmanganese complex Cp′Mn(COCOTol)(CO)(NO), in which the analogous angle is only 112°.[13] Such variation for the platinum(II) complexes might be attributed to the trans influence.[14,15] The detailed correlation is a current target of our investigation.

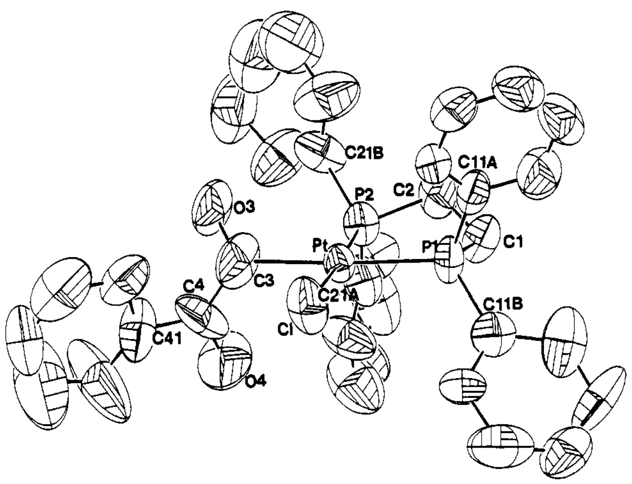

Figure 1. ORTEP drawing of complex **6**. (A drawing with complete atomic labeling is in the supplementary material.)

Solvent-Controlled Dynamic Equilibria between Complexes 3 and 6. The displacement of PPh$_3$ in complex **3** by chloride ion led to the formation of **6**. The reverse substitution was readily conducted in noncoordinating (relatively) polar solvents, such as chloroform. Their dynamic equilibrium could be shifted simply by tuning the solvent polarity. Such a chemical process has been monitored by ^{31}P NMR spectroscopy, as shown in Figure 2. Complex **3** is the only platinum species observed at the mixing of equimolar **1** and dppe in CDCl$_3$. The addition of nonpolar benzene resulted in the formation of neutral **6** at the expense of the ionic **3**. The equilibrium is shifted from **3** to the direction

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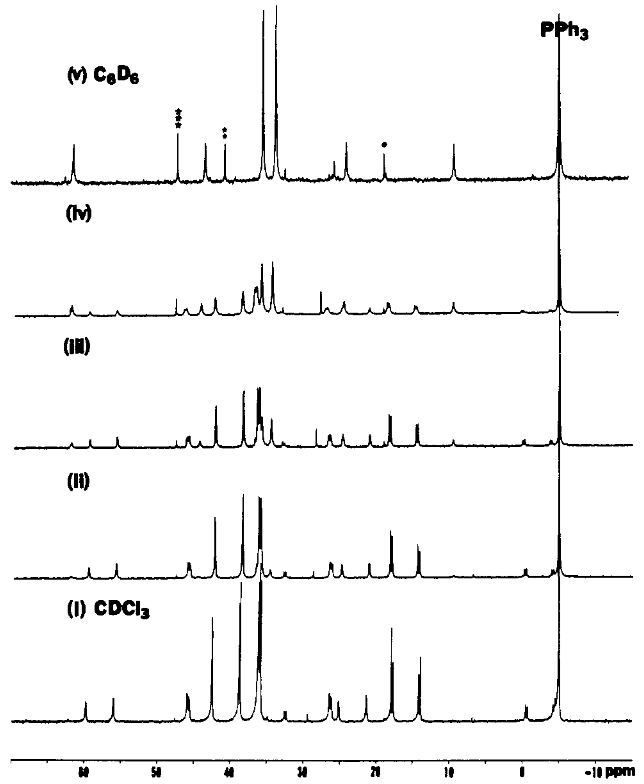


Figure 2. Solvent-controlled chemical equilibrium between complexes **3** and **6** as monitored by ^{31}P NMR spectroscopy. (Spectra are aligned with PPh_3 peaks.) Key: (i) Complex **3** and 2 equiv of PPh_3 (results from reaction of equimolar amounts of complex **1** and dppe) in $CDCl_3$; (ii) 2:1 (v/v) $CDCl_3/C_6D_6$; (iii) 1:1 (v/v) $CDCl_3/C_6D_6$; (iv) 1:2 (v/v) $CDCl_3/C_6D_6$; (v) complex **6** and 2 equiv of PPh_3 in C_6D_6. In (v), single, double, and triple asterisks indicate complexes **1**, **20**, and **21**.

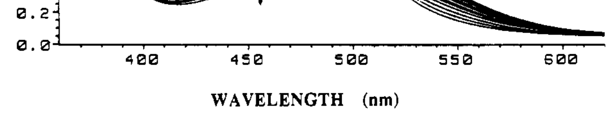
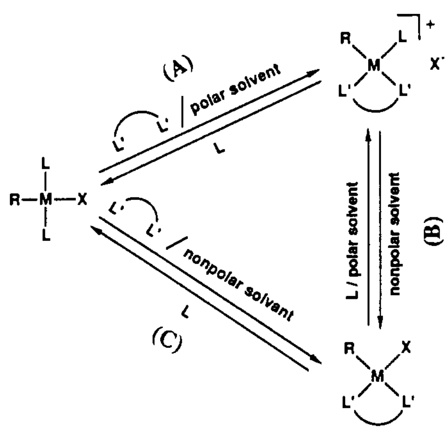


Figure 3. Spectrophotometric titration of the reaction of **6** with PPh_3 to form **3** in chloroform at 23.1 °C. $[3]_0 = 1.6 \times 10^{-2}$ mmol; $[PPh_3] = 1.6 \times 10^{-3}$ mmol/aliquot.

of **6**, when the concentration of benzene in solution increases, and vice versa. Attempts at measuring the equilibrium constants by NMR techniques were not successful, since very different signal sensitivities for the phosphorus nuclei of PPh_3 and dppe made the integration irrational.

The spectrophotometric titrations for the reaction of complex **6** with PPh_3 are shown in Figure 3, which exhibits the decay of the 456-nm band, the growth of the 504-nm band, and an isosbestic point at 512 nm, indicating a clean conversion from **6** to **3**. Besides, reactions shown in Scheme I are reversible under appropriate conditions. The addition of excess PPh_3 to a $CHCl_3$ solution of **3** caused the conversion of **3** back to **1**. Similarly, **1** could also be recovered from the reaction of **6** with excess PPh_3 in benzene. The overall relationship of the substitutions, the isomerizations, and the multiequilibria between **1**, **3**, and **6** (and **2**, **4**, and **7**) are summarized in Scheme I.

Scheme II



The substitution and isomerization reactions appear to be quite general to the d^8 square-planar monoorgano complexes. The palladium analogue *trans*-$Pd(COCOPh)(Cl)(PPh_3)_2$ (**9**) reacts with dppe or dppp in a fashion similar to that for the reactions of complex **1**, yielding *cis*-$[Pd(COCOPh)(PPh_3)(dppe)](Cl)$ (**10**) and *cis*-$Pd(COCOPh)(Cl)(dppe)$ (**11**), respectively, in different solvents. The fast phosphine exchange on the palladium complexes readily results in the formation of decarbonylated byproducts: *cis*-$[Pd(COPh)(PPh_3)(dppe)](Cl)$ and *cis*-$Pd(COPh)(Cl)(dppe)$. Reactions of *trans*-$Pt(COPh)(Cl)(PPh_3)_2$ (**12**) and *trans*-$Pt(Me)(I)(PPh_3)_2$ (**15**) with dppe also show analogous reactivity of Scheme I, affording the corresponding main products *cis*-$[Pt(COPh)(PPh_3)(dppe)]Cl$ (**13**) and $Pt(COPh)(Cl)(dppe)$ (**14**), as well as *cis*-$[Pt(Me)(PPh_3)(dppe)]I$ (**16**) and *cis*-$Pt(Me)(I)(dppe)$ (**17**). In addition, further substituted inorganic complexes $PtCl_2(dppe)$ (**18**), $[Pt(dppe)_2]Cl_2$ (**19**), and trace of other unidentified complexes were observed in greater amounts than in the reactions of (α-ketoacyl)platinum complexes. The neat transformation of **1** (or **2**) to either **3** or **6** (**4** or **7**) may be attributed to the exceptionally good trans influence of the α-ketoacyl groups,[15] which facilitate the loss of the chloride ligand.

Anderson and Cross suggested that the ligand-catalyzed cis-trans isomerizations of d^8 planar inorganic complexes, MX_2L_2, may proceed via two mechanisms. They are (1) consecutive displacement involving an ionic intermediate (eq 3) and (2) pseudorotation involving 5-coordinate intermediates (eq 4), which actually can be viewed as two extreme cases of one process. Polar solvents lead to the ionic complexes, whereas nonpolar solvents favor the 5-coordinate intermediates.[6b] Meanwhile, the reactions between the organometallic complexes $M(Ph)XL_2$ (M = Pd, Pt) and CO have also been found to form the carbonylated acyl products, analogously involving either ionic or neutral 5-coordinate species in different solvents.[9a,16] The reactions between the (α-ketoacyl)platinum complex and bidentate phosphine are now proven to occur in a similar fashion. A general scheme for a solvent-controlled substituion-isomerization process in a square-planar complex of group 10, therefore, can be illustrated in Scheme II.

In path A, polar solvents would stabilize the ionic species, $[MRL(L'\text{-}L')]X$. In the presence of excess L, the ionic species prefer to form *trans*-$MRXL_2$. On the other hand, *cis*-$MRX(L'\text{-}L')$ does exist in its pure form in polar solvents and irreversibly reacts with L to form $[MRL(L'\text{-}L')]X$. In the intermediate media, the ionic complex and the neutral species may have comparable stability, so that the equilibrium between $[MRL(L'\text{-}L')]X$ and *cis*-$MRX(L'\text{-}L')$ can be readily tuned by solvent polarity, as written in B path. In nonpolar solvents (C path), the ionic complex would be too unstable to be formed. The substitution-isomerization

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equilibrium between *trans*-$MRXL_2$ and *cis*-MRX(L′-L′) might proceed by involving 5-coordinate intermediates. There are many possible 5-coordinate intermediates. The structures containing dangling L′-L′ could be less stable. The bidentate ligands are supposed to make the pseudorotation somewhat less accessible. Besides, the nature of M, R, X, L, L′-L′, and solvents would also be influential on each equilibrium process. The determination of the exact structure of the 5-coordinate intermediates therefore would be very difficult.

Experimental Section

General Methods. The complexes *trans*-Pt(COCOPh)(Cl)$(PPh_3)_2$ (**1**),[12c] *trans*-Pt(COCOOMe)(Cl)$(PPh_3)_2$ (**2**),[12a] *trans*-Pd(COCOPh)(Cl)$(PPh_3)_2$ (**9**),[12c] *trans*-Pt(COPh)(Cl)$(PPh_3)_2$ (**12**),[19a] *trans*-Pd(COPh)(Cl)$(PPh_3)_2$ (**15**),[19b] and *trans*-Pt(Me)(I)$(PPh_3)_2$ (**17**)[19c] were prepared according to the literature methods. Other reagents were purchased and used without purification. Solvents were dried with use of standard procedures. All UV–vis spectra were recorded on a Hewlett Packard 8452A spectrophotometer. The IR spectra were recorded on a Perkin-Elmer 983G spectrophotometer. The NMR spectra were run on either a Brucker AC-E200 or a Brucker AM-300WB spectrometer. For the ^{31}P NMR spectra, the spectrometer frequency at 81.015 MHz was employed, and the chemical shifts are given in ppm (δ) relative to 85% H_3PO_4 in $CDCl_3$. Values upfield of the standard are defined as negative.

***cis*-[Pt(COCOPh)(PPh_3)(dppe)]X (X = Cl^- (3), BF_4^- (3a)).** To a $CHCl_3$ solution of complex **1** was added equimolar amounts of dppe under ambient conditions. The instantaneous appearance of a rosy color indicates the formation of **3**. Complex **3** was essentially identified by IR and NMR spectroscopy. The primary yields of **3** were estimated as >90% on the basis of ^{31}P NMR integrations. The addition of 1 equiv of $AgBF_4$ to the solution of **3** resulted in the precipitation of AgCl. The tetrafluoroborate salt **3a** could be precipitated from $CHCl_3/Et_2O$. Both **3** and **3a** were too hygroscopic to be isolated from the solvents. The conductivity of **3** was measured for a 10-mL acetonitrile solution containing 0.8 mg (0.011 mmol) of **3** and 4.6 mg (1 equiv) of dppe, on a Suntex SC-17A conductometer.

***cis*-[Pt(COCOOMe)(PPh_3)(dppe)](Cl) (4) and *cis*-[Pt(COCOPh)(PPh_3)(dppp)](Cl) (5).** Complexes **4** and **5** were respectively prepared from **2** and dppe and **1** and dppp in $CHCl_3$ according to the same procedure described above. None of them has been isolated into solid forms.

***cis*-Pt(COCOPh)(Cl)(dppe) (6), *cis*-Pt(COCOOMe)(Cl)(dppe) (7), and *cis*-Pt(COCOPh)(Cl)(dppp) (8).** The addition of large amounts of Et_2O to a solution of complex **3** resulted in the precipitation of dark orange solids of **6**. It was then purified from benzene to remove Pt(dppe)Cl_2 and [Pt$(dppe)_2$]Cl_2. The isolated yield of **6** was 86%. In an alternative preparation, 2.51 g (2.82 mmol) of complex **1** was first dissolved in 80 mL of benzene, followed by a 5-mL benzene solution containing 1.14 g (2.95 mmol) of dppe. The resulted reddish orange solution was filtered and concentrated to 15 mL. It was then transferred to 50 mL of cold *n*-hexane to crystallize the orange product. The solid complex **6** was then washed with Et_2O and was collected in a 96% yield. The procedures for the preparation of **7** and **8** were the same as those for **6**. Yellow crystalline **7** in 70% yield was isolated. Complex **8** was collected in a 91% yield as orange solids.

Dynamic Equilibrium between Complexes 3 and 6. The substitution equilibrium between complexes **3** and **6** has been monitored by ^{31}P NMR spectroscopy and UV–vis spectrophotometry. In an NMR tube, 20 mg (0.0225 mmol) of complex **1** was dissolved into 0.6 mL of $CDCl_3$. The addition of 9.0 mg (0.0225 mmol) of dppe to the solution led to the instantaneous formation of red complex **3**. After the first ^{31}P NMR spectrum was taken, the solution was concentrated to half the volume by vacuum. Into the reaction tube was first added 0.2 mL of benzene-d_6, followed by extra $CDCl_3$ to bring the total volume to 0.6 mL, giving a 2:1 v/v $CDCl_3/C_6D_6$ solution. The 1:1 v/v $CDCl_3/C_6D_6$ solution was prepared (1) by directly adding 0.2 mL of benzene-d_6 to the second solution and (2) by reversing the above procedure, beginning with 0.6 mL of benzene-d_6 containing complex **1** and dppe in the same amounts as mentioned above. The spectrophotometric titration was carried out by adding 1.59×10^{-3} mmol/aliquot of PPh_3 to a 3.0-mL $CHCl_3$ solution containing 5.3×10^{-3} M (1.59×10^{-3} mmol) **6**. The spectral scans were recorded on an HP8452A UV–vis spectrophotometer immediately after each addition.

X-ray Crystallography. Single crystals suitable for X-ray diffraction were obtained by slowly diffusing Et_2O into a concentrated CH_2Cl_2 solution of **6**. Diffraction data were measured at 300 K on a CAD-4 diffractometer with graphite-monochromatized Mo Kα radiation. Cell parameters were determined by a least-squares fit on 25 reflections at 2θ range 18–28°. Intensity data were corrected for absorption on the basis of an experimental ψ rotation curve. The refinement procedure was by a full-matrix least-squares method including all the non-hydrogen atoms anisotropically. Hydrogen atoms were fixed at the ideal geometry and C–H distance of 1.0 Å; their isotopic thermal parameters were fixed to the values of the attached carbon atoms at the convergence of the isotropic refinement. Atomic scattering factors were taken from ref 17. Anomalous dispersion corrections of Pt and Cl were applied. The space group is polar, and that the correct absolute configuration had been chosen was established by the analysis; the model reported here had $R(F) = 0.048$ and $R_w(F) = 0.033$ compared with $R(F) = 0.058$ and $R_w(F) = 0.043$ for the model of opposite chirality. Computing programs are from the NRCC SDP VAX package.[18] The final residual map contains a peak (1.6 e Å^{-3}) and a hole (−1.4 e Å^{-3}) around Pt. The detailed data are supplied in the supplementary material.

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Supplementary Material Available: Tables of complete crystal data, atomic coordinates, bond lengths and bond angles, and thermal parameters and a figure with complete atomic labeling (7 pages); a listing of structural factors (10 pages). Ordering information is given on any current masthead page.

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