Syntheses, Spectra, and Structures of (Diphosphine)platinum(II) Carbonate Complexes

Mark A. Andrews,* George L. Gould,[†] Wim T. Klooster, Kristina S. Koenig,[‡] and Eric J. Voss[§]

Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973-5000

Received March 22, 1996[⊗]

A variety of (diphosphine)platinum(II) carbonate complexes, (LL)Pt(CO_3), are readily prepared from the corresponding (diphosphine)platinum dichlorides by treatment with silver carbonate in dichoromethane solution provided that water is present. This reaction also permits facile preparation of analogous ^{13}C-labeled complexes. The carbonate ligands in these complexes have been characterized by IR and ^{13}C NMR spectroscopy. Alternative preparative routes involve conversion of the precursor dichlorides to the corresponding dialkoxides or diphenoxides, followed by treatment with water and carbon dioxide. Various reaction intermediates have been spectroscopically observed in the latter syntheses. Two crystalline modifications of ($Ph_2PCH_2CH_2CH_2PPh_2$)Pt(CO_3), one with and one without a dichloromethane of solvation, have been studied by single-crystal X-ray diffraction. Crystal data for $PtP_2O_3C_{28}H_{26}$: $P2_1/c$, $Z = 4$, $T = 200$ K, $a = 10.362(8)$ Å, $b = 14.743(6)$ Å, $c = 19.183(10)$ Å, $\beta = 122.69(6)°$. Crystal data for $PtP_2O_3C_{28}H_{26}\cdot CH_2Cl_2$: $P2_1/c$, $Z = 4$, $T \approx 298$ K, $a = 11.744(2)$ Å, $b = 15.526(3)$ Å, $c = 15.866(3)$ Å, $\beta = 101.58(1)°$.

Introduction

(Diphosphine)platinum(II) carbonate complexes, (LL)Pt(CO_3), are excellent precursors for the preparation of Pt(II) diolate and alditolate complexes,[1] as well as a number of other (LL)$Pt^{II}X_2$ and (LL)Pt^0(L′) compounds.[2] They have typically been synthesized by reaction of the corresponding dichlorides with silver carbonate[3−5] or by treatment of the corresponding dioxygen complex with carbon dioxide.[2,5−7] Difficulties we encountered in reproducing the former preparations and limitations of the latter approach led us to undertake a more detailed study. The underlying problem with the silver carbonate route has been resolved, and additional new synthetic routes have been developed. The resulting complexes have been characterized by a variety of physical techniques.

Experimental Section

General Procedures. General methods and instrumentation have been described previously.[1] Syntheses and reactions were generally conducted under argon, but synthetic workups can usually be conducted in air. Wet dichloromethane was prepared by shaking reagent grade dichloromethane with water in a separatory funnel and drawing off the bottom dichloromethane layer into a bottle for storage. Dichloromethane-d_2 was vacuum-distilled from calcium hydride. (Note: If CD_2Cl_2 is allowed to stand over CaH_2 for more than 1 or 2 d, detectable quantities of CHD_2Cl form, identified by its characteristic ^1H NMR spectrum (δ 2.99 (1:2:3:2:1 quintet, $J_{HD} = 1.6$ Hz)). Phosphines were purchased from Strem or Quantum Design. (Diphosphine)platinum(II) dichloride complexes were synthesized from K_2PtCl_4 (*caution: allergen*) by the procedure of Slack and Baird[8] or from (COD)$PtCl_2$ (COD = 1,5-cyclooctadiene) according to the procedure of Hackett and Whitesides.[9] In the latter case, it is important to add the phosphine to the COD complex and to avoid an excess of phosphine in order to prevent formation of the dicationic complex $[(LL)_2Pt^{2+}][Cl^-]_2$.[10] The dichloride complexes were optionally recrystallized by slow diffusion of hexane into a dichloromethane solution to remove traces of water and/or alcohol. Silver carbonate was prepared from silver nitrate and sodium carbonate in water, dried under vacuum, and stored protected from light. $Ag_2{}^{13}CO_3$ was purchased from Aldrich. Sodium isopropoxide was prepared by reaction in toluene of sodium metal with isopropyl alcohol that had been dried over sodium isopropoxide. Sodium *p*-methoxyphenoxide was prepared by reaction of *p*-methoxyphenol and sodium hydride in THF, followed by filtration and precipitation of the product with hexane.

Typical Silver Carbonate Reaction: Synthesis of (dppp)Pt(CO_3). Solid Ag_2CO_3 (410 mg, 1.487 mmol, 1.22 equiv) was added to a solution of ($Ph_2PCH_2CH_2CH_2PPh_2$)$PtCl_2$ (825 mg, 1.216 mmol) in a minimum volume of wet CH_2Cl_2 (125 mL) without any attempt to exclude air. The reaction mixture was wrapped with aluminum foil and stirred for 3 h, at which time a ^{31}P NMR spectrum showed that the reaction was complete. The solution was filtered through a fine-porosity frit, and the solids were washed with CH_2Cl_2 (3 × 5 mL). The filtrate and washes were then concentrated to approximately 20 mL, and hexane (20 mL) was added. The resulting white crystalline precipitate was collected using a fine-porosity frit under slight vacuum and dried under high vacuum to give pure (dppp)$PtCO_3$ (700 mg, 88% yield), identified by comparison of ^{31}P and ^1H NMR data with those of an authentic sample.[1]

The complexes ($(Ph_3P)_2$)Pt(CO_3), (dppe)Pt(CO_3), (dppb)Pt(CO_3), (dcpe)Pt(CO_3), (dtpe)Pt(CO_3), (dppv)Pt(CO_3), and (dppz)Pt(CO_3) were prepared by a similar procedure, with synthesis times varying from 1 to 24 h. Definitions of phosphine abbreviations, reaction yields, and spectral data for these complexes are found in Table 1. Details of syntheses are provided in the Supporting Information.

^{13}C-Labeled Complexes. ^{13}C-labeled platinum carbonate complexes were prepared analogously by employing $Ag_2{}^{13}CO_3$.

[†] Present address: Department of Chemistry, M/C 111, University of Illinois, P.O. Box 4348, Chicago, IL 60680.

[‡] Present address: Pharmacia & Upjohn Inc., 1500-91-2, Kalamazoo, MI 49001.

[§] Present address: Department of Chemistry, Southern Illinois University, Edwardsville, IL 62026-1652.

[⊗] Abstract published in *Advance ACS Abstracts,* August 15, 1996.

(1) Andrews, M. A.; Voss, E. J.; Gould, G. L.; Klooster, W. T.; Koetzle, T. F. *J. Am. Chem. Soc.* **1994**, *116*, 5730−5740.

(2) Blake, D. M.; Roundhill, D. M. *Inorg. Synth.* **1978**, *18*, 120−124.

(3) Anderson, G. K.; Lumetta, G. J.; Siria, J. W. *J. Organomet. Chem.* **1992**, *434*, 253−259.

(4) Goldsworthy, D. H.; Hartley, F. R.; Marshall, G. L.; Murray, S. G. *Inorg. Chem.* **1985**, *24*, 2849−2853.

(5) Hayward, P. J.; Blake, D. M.; Wilkinson, G.; Nyman, C. J. *J. Am. Chem. Soc.* **1970**, *92*, 5873−5878.

(6) Scherer, O. J.; Jungmann, H.; Hussong, K. *J. Organomet. Chem.* **1983**, *247,* C1-C4.

(7) Nyman, C. J.; Wymore, C. E.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 561−563.

(8) Slack, D. A.; Baird, M. C. *Inorg. Chim. Acta* **1977**, *24*, 277−280.

(9) Hackett, M.; Whitesides, G. *J. Am. Chem. Soc.* **1988**, *110*, 1449−1462.

(10) Cf.: Anderson, G. K.; Davies, J. A.; Schoeck, D. J. *Inorg. Chim. Acta* **1983**, *76*, L251−L252.

S0020-1669(96)00315-1 CCC: $12.00

Table 1. Synthetic and Spectroscopic Data for (LL)Pt(CO_3) Complexes

LL[a]	synth method[b] (yield/%)	δ (^{31}P)[c] (J_{PtP}/Hz)	δ ($^{13}CO_3$)[c] (J_{PtC}, J_{PC}/Hz)	$\nu_{C=O}$ and $2\delta_{CO}$[d]/cm^{-1}
$(PPh_3)_2$	Ag (71)	7.1 (3697)	166.9 (66, 4)	1675, 1631
dppm	OAr (41)	−59.7 (3005)		
dppe	Ag (83)	32.8 (3518)	168.4 (60, 4)	1675, 1617
	OR (85)			
dppp	Ag (88)	−12.0 (3377)	167.6 (61, 4)	1661, 1627
	OR (85)			
dppb	Ag (88)	2.4 (3509)		1660, 1624
	OAr (99)			
dtpe	Ag (90)	31.4 (3518)	168.7 (60, 4)	1687, 1662
dcpe	Ag (85)	58.7 (3429)	169.4 (54, 4)	1652, 1629
	OR (87)			
dppv	Ag (100)	39.9 (3534)	168.3 (58, 4)	
dppz	Ag (76)	32.9 (3503)		

[a] dppm = bis(diphenylphosphino)methane, dppe = 1,2-bis(diphenylphosphino)ethane, dppp = 1,3-bis(diphenylphosphino)propane, dppb = 1,4-bis(diphenylphosphino)butane, dtpe = 1,2-bis(di-*p*-tolylphosphino)ethane, dcpe = 1,2-bis(dicyclohexylphosphino)ethane, dppv = *cis*-1,2-bis(diphenylphosphino)ethene, dppz = 1,2-bis(diphenylphosphino)benzene. [b] Ag = Ag_2CO_3, OR = NaO-*i*-Pr, OAr = $NaOC_6H_4OMe$. [c] CD_2Cl_2 solution. [d] Nujol mull

Typical Isopropoxide Reaction: Synthesis of (dcpe)Pt(CO_3). Sodium chloride (5 mg, to seed crystallization of NaCl, fostering formation of larger crystals to facilitate filtration) and (dcpe)$PtCl_2$ (1.00 g, 1.45 mmol) were dissolved/suspended in THF (~60 mL) under argon. Sodium isopropoxide (0.268 g, 3.27 mmol, 2.25 equiv) was then added in aliquots over a period of 5−10 min with stirring. After 4 d, a ^{31}P NMR spectrum of an aliquot showed that the reaction to give (dcpe)Pt(O-*i*-Pr)$_2$ (δ 48.4 (J_{PtP} = 3315 Hz)) was complete. The reaction mixture was filtered through a dried, fine frit under slight positive pressure to give a clear orange solution. Water (130 μL, 7.2 mmol, 5 equiv/Pt) was added and the stirred solution promptly bubbled with carbon dioxide. Within 1 min, a copious white precipitate formed. The flask was capped under carbon dioxide and allowed to stir overnight, after which the precipitate was isolated by centrifugation in air, washed with ether (3 × 5 mL), and dried under vacuum to give (dcpe)Pt(CO_3) (0.856 g, 87%).

The complexes (dppe)Pt(CO_3) and (dppp)Pt(CO_3),were prepared by a similar procedure, formation of the isopropoxide complexes being complete in 3 h. Details are provided in the Supporting Information.

Typical Phenoxide Reaction: Synthesis of (dppb)Pt(CO_3). Sodium chloride (27 mg) and (dppb)$PtCl_2$ (1.013 g, 1.46 mmol) were dissolved/suspended in THF (~60 mL). Sodium *p*-methoxyphenoxide (451.8 mg, 3.09 mmol, 2.11 equiv) was added in portions with stirring. A ^{31}P NMR spectrum taken of the resulting bright yellow solution after 2 h showed complete conversion to (dppb)Pt(OC_6H_4OMe)$_2$ (δ 3.7, J_{PtP} = 3488 Hz). The reaction mixture was then filtered through a fine frit with the aid of Celite. The clear filtrate was treated with water (140 μL, 5 equiv) and the stirred solution promptly bubbled with carbon dioxide. The flask was capped under carbon dioxide and allowed to stir overnight, during which a white precipitate formed. The precipitate was isolated by centrifugation in air, washed with ether (3 × 10 mL) and dried under vacuum to give (dppb)Pt(CO_3) (0.987 g, 99%).

Synthesis of (dppm)Pt(CO_3). A. Ag_2CO_3 Method. Treatment of ($Ph_2PCH_2PPh_2$)$PtCl_2$ (248 mg, 384 μmol) with Ag_2CO_3 (130 mg, 471 μmol, 1.23 equiv) in wet dichloromethane (40 mL) for 1 h gave ca. 80−85% conversion to the desired carbonate. By 5 h, decomposition reactions had set in and workup of the reaction by concentration and precipitation with hexane yielded a product (189 mg) that contained only about 15% (dppm)Pt(CO_3) (identified by comparison of ^{31}P NMR data with those of an authentic sample; vide infra). Two other significant products were present. The major product (ca. 65%) exhibited the splitting pattern of an AB spin system in the ^{31}P NMR spectrum (CD_2Cl_2) at δ 23.0 (J_{PtP} = 3511 Hz) and 1.8 (J_{PtP} = 4211 Hz) with J_{PP} = 29 Hz. The minor product (ca. 20%) also exhibited the splitting pattern of an AB spin system at δ 25.0 (J_{PtP} = 3434 Hz) and 0.6 (J_{PtP} = 4304 Hz) with J_{PP} = 29 Hz. A ^1H NMR spectrum showed doublets (J_{PH} = 12 Hz) with shoulders attributed to ^{195}P satellites for the P−CH_2 groups of the unknown products at δ 2.22 (major) and δ 2.15 (minor) (about 2.5 ppm upfield of the "triplet" due to the P−CH_2 group of (dppm)Pt(CO_3)), as well as a peak at δ −1.42 attributed to a platinum hydride (d, J_{PH} = 1 Hz (J_{PtH} = 410 Hz)) whose area was approximately equal to that of the CH_2 group of the minor product.

B. Phenoxide Method. The complex (dppm)$PtCl_2$ (251.9 mg, 387.3 μmol), *p*-$NaOC_6H_4OCH_3$ (204.9 mg, 1402 μmol, 3.6 equiv), and NaCl (35 mg) were dissolved/suspended in THF (20 mL) under argon in a 25 mL screw-capped Erlenmeyer flask. The solution turned bright yellow, and after 3 h, ^{31}P NMR spectroscopy confirmed that conversion to (dppm)Pt($OC_6H_4OCH_3$)$_2$ (δ −67.8 (J_{PtP} = 2912 Hz)) was complete. The solution was filtered through a 3 cm Celite pad in air to remove the NaCl, and the pad was washed with THF (25 mL to load, 3 × 5 mL washes). Water (250 μL, 36 equiv) was added to the filtrate, and the solution was immediately bubbled with CO_2 for 5 min. The solution turned tan, and cream-colored solids began to form. The 100 mL flask containing this mixture was capped under CO_2, and the solution was stirred for 2 h. The solid product was isolated by centrifugation, washed with Et_2O (5 mL), water (1 mL), and Et_2O (2 × 5 mL), and vacuum-dried; crude yield = 204 mg (82%). Solids insoluble in CH_2Cl_2 were still present (presumably NaOH), so the product was dissolved in CH_2Cl_2 (15 mL) and the resulting solution filtered through a 1 cm Celite pad. Cream-colored (dppm)Pt(CO_3) was precipitated from the filtrate by addition of Et_2O (20 mL), isolated by centrifugation, washed with Et_2O (3 × 5 mL), and vacuum-dried. Isolated yield = 102 mg (41%). ^1H NMR (CD_2Cl_2): δ 7.80 (m, 8 H, Ph), 7.50 (m, 12 H, Ph), 4.63 (t, J_{PH} = 11 Hz, J_{PtH} = 56 Hz, 2 H, PCH_2). Anal. Calcd (found) for $C_{26}H_{22}O_3P_2Pt$: C, 48.83 (48.82); H, 3.47 (3.64).

Study of Reaction Intermediates in the (dcpe)Pt Isopropoxide System. THF (1.955 g, 2.21 mL) was added to (dcpe)$PtCl_2$ (26.8 mg, 39.5 μmol) and sodium isopropoxide (3.2 mg, 39 μmol, 0.99 equiv) in a screw-capped Erlynmeyer flask under argon in a glovebox and the reaction mixture stirred. After 1.5 h, one-third of the solution (0.660 g, 13 μmol of Pt) was transferred to a screw-capped 5 mm NMR tube and examined by ^{31}P NMR spectroscopy at both 1.75 and 16 h. The solution composition was determined to be about 11% (dcpe)$PtCl_2$ (δ 64.9 (J_{PtP} = 3539 Hz)), 87% (dcpe)Pt(Cl)(O-*i*-Pr) (δ 61.5 (J_{PtP} = 4026 Hz), 52.6 (J_{PtP} = 2988 Hz), J_{PP} = 2.7 Hz), and 2% (dcpe)Pt(O-*i*-Pr)$_2$. Water (0.3 μL, 17 μmol, 1.3 equiv) was then added and the reaction monitored vs time by ^{31}P NMR. After 20 min, about 10% of the (dcpe)Pt(Cl)(O-*i*-Pr) complex had hydrolyzed to (dcpe)Pt(Cl)(OH), and after 23 h, the solution composition was determined to be about 7% (dcpe)$PtCl_2$, 3% (dcpe)Pt(Cl)(O-*i*-Pr), 87% (dcpe)Pt(Cl)(OH) (δ 61.8 (J_{PtP} = 3915 Hz), 54.1 (J_{PtP} = 2970 Hz), J_{PP} = 2.7 Hz), and 3% (dcpe)Pt(OH)$_2$.

Additional sodium isopropoxide (2.3 mg, 28 μmol, total 2.05 equiv/Pt) was added to the remaining two-thirds of the reaction mixture in the Erlynmeyer flask and the mixture stirred for 24 h. An aliquot (0.602 g, 13 μmol Pt) was then transferred to a screw-capped 5 mm NMR tube and examined by ^{31}P NMR spectroscopy, showing essentially complete conversion to (dcpe)Pt(O-*i*-Pr)$_2$ (δ 48.4 (J_{PtP} = 3315 Hz)). Water (0.3 μL, 17 μmol, 1.3 equiv/Pt) was then added and the reaction monitored vs time by ^{31}P NMR. After 30 min, about 15% of the (dcpe)Pt(O-*i*-Pr)$_2$ complex had hydrolyzed to (dcpe)Pt(O-*i*-Pr)(OH), and after 24 h, the solution composition was determined to be about 4% (dcpe)Pt(O-*i*-Pr)$_2$, 42% (dcpe)Pt(O-*i*-Pr)(OH) (δ 52.6 (J_{PtP} = 3267 Hz), 49.7 (J_{PtP} = 3301 Hz), J_{PP} = 1.8 Hz), 45% (dcpe)Pt(OH)$_2$ (δ 53.0 (J_{PtP} = 3241 Hz)), 6% (dcpe)Pt(Cl)(OH), and 2% (dcpe)$PtCl_2$. (Note: Near-stoichiometric quantities of water were used in these studies to minimize the effect of hydrogen-bonding by excess water on the ^{31}P chemical shifts and on the Pt−P coupling constants.[1] Under the conditions used here, the peak positions and couplings for compounds that could be observed in both the absence and the presence of water agreed within 5 Hz.)

Reaction of (dppp)Pt(CO_3) with (PPN)Cl. The complex (dppp)Pt(CO_3) (6.2 mg, 9.3 μmol) and $[(Ph_3P)_2N^+][Cl^-]$ ((PPN)Cl (22.2 mg, 38.7 μmol, 4.2 equiv; vacuum-dried at 100 °C)) were nearly dissolved in CD_2Cl_2 (0.65 mL) in a screw-capped 5 mm NMR tube under argon. ^{31}P NMR spectra taken at both 1.25 and 20 h showed that the solution composition was approximately 90% (dppp)Pt(CO_3) and 10% (dppp)$PtCl_2$. Five hours after addition of water (1 μL), a ^{31}P NMR spectrum showed that the solution composition was now 86% (dppp)Pt(CO_3) and 14% (dppp)$PtCl_2$.

Reaction of (dppp)PtCl$_2$ with PPh$_2$Bn. The complex (dppp)PtCl$_2$ (9.0 mg, 13.3 μmol) and benzyldiphenylphosphine (PPh$_2$Bn, 6.1 mg, 22.1 μmol, 1.7 equiv) were dissolved in CD$_2$Cl$_2$ in a screw-capped 5 mm NMR tube under argon. ^{31}P NMR spectra taken at both 0.5 and 4 h showed, in addition to free PPh$_2$Bn, that the solution composition was approximately 25% (dppp)PtCl$_2$ and 75% [(dppp)Pt(PPh$_2$Bn)Cl$^+$][Cl$^-$]. (The latter complex was identified by its characteristic ^{31}P NMR spectrum (δ 17.9 (dd, $J_{PP} = 388$, 16 Hz, $J_{PtP} = 2409$ Hz), -0.4 (dd, $J_{PP} = 388$, 30 Hz, $J_{PtP} = 2268$ Hz), -1.9 (dd, $J_{PP} = 30$, 16 Hz, $J_{PtP} = 3435$ Hz)), analogous to that of closely related complexes.[11−13]) After addition of water (5 μL), ^{31}P NMR spectra taken at both 2 and 20 h showed that the solution Pt composition had shifted to 9% (dppp)PtCl$_2$ and 91% [(dppp)Pt(PPh$_2$Bn)Cl$^+$][Cl$^-$].

X-ray Crystal Structure Determinations. A. (dppp)Pt(CO$_3$). Crystals of (dppp)Pt(CO$_3$) were obtained by carefully layering a dichloromethane solution of the compound with ether to permit slow diffusion to occur. X-ray diffraction data were obtained with an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo Kα radiation. The crystal system was monoclinic, and from the systematic absences, the space group was unambiguously determined to be $P2_1/c$. The cell parameters were obtained by a least-squares fit of $\sin^2\theta$ values for 25 reflections in the range $8° < \theta < 10°$, each of which was measured at two equivalent positions (one with positive θ and one with negative θ). Integrated intensities were measured by $\omega/2\theta$ scans with an ω-scan width of $(1.00 + 0.35 \tan\theta)°$, using varying scan speeds determined by a prescan. Lorentz, polarization, and absorption corrections were applied, the last based on ψ scans.[14] A partial structure was found using direct methods.[15] All remaining non-hydrogen atoms were found in successive difference maps after refinements by difference Fourier methods.[16] The positional and isotropic displacement parameters so obtained were then used as starting input to a full-matrix, least-squares refinement.[17] Atomic positional and anisotropic displacement parameters were varied, together with the scale factor, converging with $\Delta/\sigma < 0.01$. The extinction correction was omitted after the extinction coefficient failed to assume a significant value.[18] The quantity minimized was $\sum w||F_o| - |F_c||^2$ with weights $w = 1/\sigma^2(F_o)$ and $\sigma^2(F_o) = \sigma_{cs}^2 + (0.02F_o)^2$, where σ_{cs}^2 is the variance due to counting statistics. Atomic scattering factors were those as calculated by Cromer and Waber.[19] Anomalous dispersion corrections were included.[20] Residual maxima in the final difference Fourier map were ±2% near and relative to the Pt atom. Crystallographic data and selected bond distances and angles are given in Tables 2−4. Additional crystallographic details are provided in the Supporting Information. An ORTEP[21] drawing is shown in Figure 1 (left).

B. (dppp)Pt(CO$_3$)·CH$_2$Cl$_2$. Crystals of (dppp)Pt(CO$_3$)·CH$_2$Cl$_2$ were obtained in the course of trying to crystallize (dppp)Pt(1,2,4-butanetriolate).[1] After multiple crystallizations from dichloromethane−ether, the dichloromethane solvate of the carbonate complex was obtained as determined by the subsequent X-ray structural study. The crystal system, space group, and cell parameters were obtained as described above, the last values from 25 reflections in the range $10° < \theta < 15°$. Data collection, corrections, and structure refinement were the same as described above. Residual maxima in the final difference Fourier map were ±1% near and relative to the Pt atom. Crystallographic data and selected bond distances and angles are given in Tables 2−4. Additional crystallographic details are provided in the Supporting Information. An ORTEP drawing is shown in Figure 1 (right).

Table 2. Crystallographic Data for (dppp)Pt(CO$_3$) and (dppp)Pt(CO$_3$)·CH$_2$Cl$_2$[a]

	(dppp)Pt(CO$_3$)	(dppp)Pt(CO$_3$)·CH$_2$Cl$_2$
formula	PtP$_2$O$_3$C$_{28}$H$_{26}$	PtP$_2$O$_3$C$_{28}$H$_{26}$·CH$_2$Cl$_2$
fw	667.56	752.50
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a/Å	10.362(8)	11.744(2)
b/Å	14.743(6)	15.526(3)
c/Å	19.183(10)	15.866(3)
β/deg	122.69(6)	101.58(1)
V/Å^3	2466.3(14)	2834.1(8)
Z	4	4
T/K	200	∼298
λ/Å	0.710 69	0.710 69
ρ_{calcd}/g cm^{-3}	1.798	1.763
μ/cm^{-1}	61.4	55.4
$R(F_o)^b$	0.0781	0.0714
$R_w(F_o)^c$	0.0766	0.0586

[a] Numbers given in parentheses in this and subsequent tables are estimated standard deviations in the least significant digit(s). [b] $R(F_o) = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w(F_o) = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$.

Table 3. Selected Distances (Å) in (dppp)Pt(CO$_3$)

	w/o DM[a]	w DM[b]		w/o DM[a]	w DM[b]
Pt−P1	2.216(5)	2.226(6)	C1−O3	1.228(18)	1.290(25)
Pt−P2	2.214(5)	2.220(5)	P1−C2	1.802(16)	1.820(24)
Pt−O1	2.063(11)	2.052(14)	P2−C4	1.828(17)	1.826(24)
Pt−O2	2.075(11)	2.066(13)	C2−C3	1.561(33)	1.425(33)
C1−O1	1.354(24)	1.341(26)	C3−C4	1.554(23)	1.456(40)
C1−O2	1.332(22)	1.313(29)			

[a] Structure without dichloromethane solvate. [b] Structure with solvate.

Table 4. Selected Angles (deg) in (dppp)Pt(CO$_3$)

	w/o DM[a]	w DM[b]		w/o DM[a]	w DM[b]
P1−Pt−P2	96.0(2)	95.5(2)	O1−C1−O2	112.5(13)	116.6(17)
P1−Pt−O2	101.1(3)	99.8(4)	O1−C1−O3	123.2(17)	120.6(21)
P2−Pt−O1	97.5(4)	98.3(4)	O2−C1−O3	124.3(18)	122.7(20)
O1−Pt−O2	65.3(5)	66.5(5)	Pt−P1−C2	119.6(7)	120.9(8)
P1−Pt−O1	166.4(4)	166.3(4)	Pt−P2−C4	119.1(7)	121.4(7)
P2−Pt−O2	162.9(3)	164.7(4)	P1−C2−C3	115.5(15)	115.5(20)
Pt−O1−C1	91.1(10)	88.3(12)	P2−C4−C3	111.0(12)	114.0(18)
Pt−O2−C1	91.0(10)	88.5(11)	C2−C3−C4	110.3(15)	128.2(24)

[a] Structure without dichloromethane solvate. [b] Structure with solvate.

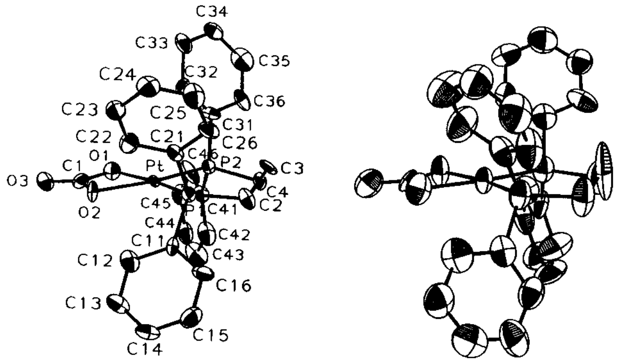


Figure 1. ORTEP drawings (50% probability level) of (dppp)Pt(CO$_3$) (left) and (dppp)Pt(CO$_3$)·CH$_2$Cl$_2$ (right). Atom labels for the two structures are the same.

---

(11) Oliver, D. L.; Anderson, G. K. *Polyhedron* **1992**, *11*, 2415−2420.

(12) Anderson, G. K.; Lumetta, G. J. *Inorg. Chem.* **1987**, *26*, 1518−1524.

(13) Davies, J. A.; Hartley, F. R.; Murray, S. G. *Inorg. Chem.* **1980**, *19*, 2299−2303.

(14) Fair, C. K. *MolEN. An Interactive Intelligent System for Crystal Analysis*; Enraf-Nonius: Delft, The Netherlands, 1990.

(15) Gilmore, G. J. *MITHRIL. A Computer Program for the Automatic Solution of Crystal Structures from X-ray Data*; Department of Chemistry, University of Glasgow: Glasgow, Scotland, 1983.

(16) Sheldrick, G. M. *SHELX-76*: *Program for Crystal Structure Determination*; University of Cambridge: Cambridge, England, 1976.

(17) Craven, B. M.; Weber, H. P.; He, X. M. *The POP Least-Squares Refinement Procedure*; University of Pittsburgh: Pittsburgh, PA, 1987.

(18) Becker, P. J.; Coppens, P. *Acta Crystallogr., Sect. A* **1974**, *30*, 129−147.

(19) Cromer, D. T.; Waber, J. T. In *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 71−147.

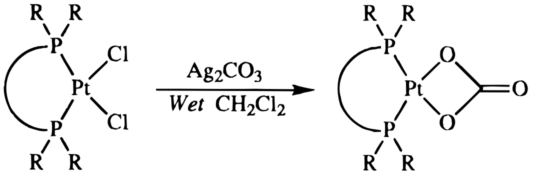
(20) Cromer, D. T.; Ibers, J. A. In *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 148−151.

(21) Johnson, C. K. ORTEPII. Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

Results and Discussion

Syntheses. (LL)Pt(CO_3) complexes have been known for some time, generally having been prepared either from (LL)Pt(O_2) and CO_2[2,5–7] or from (LL)PtCl_2 and Ag_2CO_3.[3–5] Platinum carbonate complexes have also been observed to form from adventitious "decomposition" reactions of platinum hydride complexes[22,23] or, more recently, from reactions of hydroxide or oxalate complexes.[3,24–26] The (LL)Pt(O_2) route to carbonate complexes did not appear to offer the generality that we needed, particularly for future studies with other metals. In addition, the dioxygen complexes require a multistep synthesis from standard platinum starting materials. The simplicity and potential generality of the metal chloride + silver carbonate route to carbonate complexes was appealing, but our initial attempts to reproduce these preparations led to only slow, partial conversion to the desired product. We therefore conducted a detailed study of the synthesis of these complexes, resulting in both new and improved preparations and a number of new complexes (Table 1).

No reaction at all occurs between (dppe)PtCl_2 and Ag_2CO_3 in dichloromethane over a period of 24 h when the reagents and solvents are rigorously anhydrous. With reagent grade dichloromethane off the shelf, the reaction went to completion, but took 3 days. An attempt was made to catalyze the reaction by the addition of triphenylphosphine, which is known to displace a chloride ion from (LL)PtCl_2 to form $[(LL)PtL'Cl]^+$ species.[12,13] Catalysis was indeed observed, but isolation of the product carbonate was then complicated by solubilization of the silver chloride byproduct through complexation with the triphenylphosphine.[27] The observation that water enhances the formation of the above mentioned $[(LL)PtL'Cl]^+$ species (see Experimental Section) suggested that water might also enhance the silver carbonate reaction. This led to the discovery that conversion of (dppe)PtCl_2 to (dppe)Pt(CO_3) by the action of silver carbonate is complete in only 3 h at room temperature when the dichloromethane is saturated with water (eq 1).

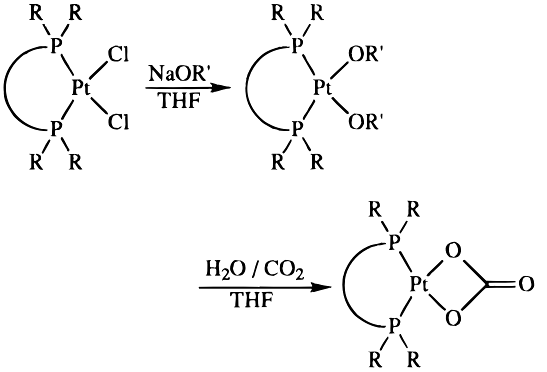


(1)

This route is the preferred method for preparing these complexes; yields are generally in excess of 80%. Use of commercially available $Ag_2{}^{13}CO_3$ allows preparation of corresponding isotopically labeled complexes, which has facilitated IR and NMR spectroscopic characterization of the carbonate ligand. The greatest drawback is the large volume of solvent often required because of the low solubility of most of the starting chlorides and product carbonates. This synthetic method was recently successfully extended to the preparation of the palladium complexes (dppp)Pd(CO_3) and (dcpe)Pd(CO_3).[28]

Of the (diphosphine)platinum(II) chlorides treated with silver carbonate to date, the only ones that have failed to give the corresponding carbonate in good yield have been (dppm)PtCl_2, $((C_6F_5)_2PCH_2CH_2P(C_6F_5)_2)PtCl_2$ ($(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$ = dfppe), and $(Me_2PCH_2CH_2PMe_2)PtCl_2$. For dppm, decomposition of the product carbonate is competitive with its formation. The two major decomposition products have not been identified, but both no longer appear to have a chelated dppm ligand since the ^{31}P chemical shifts are now in the range 0−25 ppm rather than the ca. −60 ppm region typically observed for chelated dppm.[29] Futhermore, ^1H NMR suggests that one of these products is a platinum hydride complex (δ −1.42 (d (J_{PH} = 1.3 Hz), J_{PtH} = 410 Hz)). Details of the reactions involving the latter chlorides can be found in the Supporting Information.

Prior to solving the problems associated with the silver carbonate route, we examined the hydrolysis of (LL)Pt(alkoxide)$_2$ complexes in the presence of carbon dioxide as a synthetic method (eq 2). This new technique worked well for the preparation of (dppp)Pt(CO_3) and (dcpe)Pt(CO_3), provided that the solvent employed dissolves the sodium isopropoxide (e.g., THF) and that the resulting solutions are filtered to remove the precipitated NaCl before treatment with water and carbon dioxide. The desired product precipitates out in good yield. For other phosphines, i.e., dppe and especially dppm, colored byproducts were often observed in the preparation of the intermediate isoproxide complexes. This is presumably due to β-hydrogen elimination reactions to give Pt(0)-derived complexes, as observed for (dppe)Pt(OMe)$_2$.[30] Furthermore, similar problems were observed in attempts to prepare palladium carbonate complexes.[31] The use of alkoxides lacking β-hydrogens was therefore investigated. Serious decomposition problems were encountered with potassium *tert*-butoxide, even with (dppp)PtCl_2, perhaps due to the high basicity and reduction potential of *tert*-butoxide or to the generation of unstable platinum hydroxide complexes from the *tert*-butoxide.[32,33] The less basic potassium trimethylsiloxide proved more successful, but different problems ensued.[31,34,35] The most successful variation on this approach employed phenoxides. The *p*-methoxy derivative was chosen to minimize the acidity of the product phenol on hydrolysis, since such acidity could either inhibit the hydrolysis or lead to strong hydrogen bonding of



(2)

---

(22) Robertson, G. B.; Tucker, P. A. *Acta Crystallogr.* **1983**, *C39*, 858−860.

(23) Davies, J. A.; Eagle, C. T.; Pinkerton, A. A.; Syed, R. *Acta Crystallogr.* **1987**, *C43*, 1547−1549.

(24) Miyamoto, T. K.; Suzuki, Y.; Ichida, H. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 3386−3397.

(25) Porta, F.; Ragaini, F.; Cenini, S.; Sciacovelli, O.; Camporeale, M. *Inorg. Chim. Acta* **1990**, *173*, 229−235.

(26) Olgemöller, B.; Olgemöller, L.; Beck, W. *Chem. Ber.* **1981**, *114*, 2971−2978.

(27) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry: A Comprehensive Text*, 3rd ed.; Interscience: New York, 1972; pp 1047−1048.

(28) Koenig, K. S.; Mandal, S. K. Unpublished results.

(29) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229−266.

(30) Bryndza, H. E.; Calabrese, J. C.; Marsi, M.; Roe, D. C.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 4805−4813.

(31) Gould, G. L. Unpublished results.

(32) Ladipo, F. T.; Kooti, M.; Merola, J. S. *Inorg. Chem.* **1993**, *32*, 1681−1688.

(33) Woerpel, K. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 7888−7889.

(34) Andrews, M. A.; Gould, G. L.; Voss, E. J. *Inorg. Chem.* **1996**, *35*, 5740−5742.

(35) Andrews, M. A.; Gould, G. L. *Organometallics* **1991**, *10*, 387−389.

the phenol to the product carbonate.[1,36] This route worked well in the few cases tried and is, in fact, the only method we have found to prepare pure (dppm)Pt(CO_3). Interestingly, reaction of (dppm)$PtCl_2$ with sodium *p*-methoxyphenoxide required at least 3 equiv of phenoxide rather than the expected 2 equiv to give complete conversion to (dppm)Pt$(OAr)_2$. It is possible that this is due to deprotonation of the dppm methylene carbon to give $[(Ph_2PCHPPh_2)Pt(OAr)_2]^-$, which is reprotonated upon hydrolysis and carboxylation.[37]

Reaction Intermediates. While this work was in progress, the synthesis of $(Me_3P)_2Pt(OH)_2$ from the corresponding dinitrate complex was reported, along with its reaction with carbon dioxide to give $(Me_3P)_2Pt(CO_3)$.[24] Such hydroxide complexes are undoubtedly intermediates in our alkoxide-mediated carbonate syntheses as well. Indeed, a number of intermediates and hydrolysis products can be observed during the reaction of (LL)-$PtCl_2$ with alkoxide anions and water, including species assigned to be (LL)Pt(O-*i*-Pr)(Cl), (LL)Pt(OH)(Cl), (LL)Pt$(O\text{-}i\text{-}Pr)_2$, (LL)-Pt(O-*i*-Pr)(OH), and (LL)Pt$(OH)_2$ on the basis of ^{31}P NMR data and the systematic variation of solution composition as a function of reaction stoichiometry and the intentional addition of water. A representative ^{31}P NMR study is given in the Experimental Section for the (dcpe)Pt series. A characteristic feature observed for all the asymmetric (LL)Pt(Cl)(OR) complexes is the accentuated difference between the values of the two $^{195}Pt-^{31}P$ coupling constants compared to the values found for the corresponding symmetrical complexes. Thus $J_{PtP} = 3539$ Hz for (dcpe)$PtCl_2$ and 3315 Hz for (dcpe)Pt$(O\text{-}i\text{-}Pr)_2$, while (dcpe)Pt(O-*i*-Pr)(Cl) has $J_{PtP} = 4026$ and 2988 Hz.

NMR Spectral Data. Selected ^{31}P and ^{13}C NMR spectral data for the carbonate complexes are given in Table 1. The $^{195}Pt-^{31}P$ coupling constants are intermediate between those observed for the corresponding dichloride and dialkoxide complexes. The ^{13}C chemical shifts of these platinum complexes (165−170 ppm), determined here for the first time, fall in the same range as those previously observed for (ammine)-Co^{III}(carbonate) complexes[38,39] and for carbonyl phosphine carbonate complexes of tungsten and ruthenium.[40] Coupling of the carbonate carbon to both ^{195}Pt and ^{31}P is observed ($^2J_{PtC} \approx 60$ Hz, $^3J_{PC} \approx 4$ Hz).

Vibrational Spectra. The vibrational spectroscopy of metal carbonate complexes, such as $[Co^{III}(NH_3)_4(CO_3)]^+$, has in principle been rather well-investigated[41−47] and includes two normal-coordinate analyses.[48,49] Surprisingly though, these have not been confirmed by isotopic labeling. One synthetic study has reported IR data for $(Ph_3P)_2Pt(CO_3)$ complexes derived from labeled dioxygen containing significant amounts of all three stable oxygen isotopes (^{16}O, ^{17}O, and ^{18}O).[25] The reported band shifts are inexplicably small, i.e., only 5−10 cm^{-1}. We had hoped that infrared spectra of the fully-labeled ^{13}C carbonate complexes prepared in the present work would clarify and confirm the previous metal carbonate vibrational studies. Instead, more anomalous findings emerged. First is the multiplicity of bands observed between 1600 and 1700 cm^{-1}, both in the solid state (Nujol mull and KBr disk) and in solution ($CDCl_3$): 1675 (vs) and 1631 (m) cm^{-1} for $(Ph_3P)_2Pt(CO_3)$ and 1644 (sh), 1631 (vs), 1581 (m), and 1570 (m) cm^{-1} for $(Ph_3P)_2$-Pt($^{13}CO_3$); see Supporting Information for illustrative spectra. Only one fundamental carbonate vibrational mode is expected in this region, namely the C═O stretch.[47] The extra band or bands are plausibly attributed to an overtone of the out-of-plane carbonate bending mode at 818 (m) cm^{-1} ($2 \times 818 = 1636 \approx 1631$ cm^{-1}) whose intensity is enhanced by Fermi resonance with the C═O stretch (1675 cm^{-1}). More disturbing is the large isotope shift observed for these bands, as much as 45−50 cm^{-1}. This is more than the ca. 37 cm^{-1} expected for an isolated C═O oscillator with a vibrational frequency of 1675 cm^{-1} for the $^{12}C═^{16}O$ species. We considered the possibility that these anomalous results were due to the presence of complexes containing ^{18}O-labeled species as well as ^{13}C-labeled species, as this could explain both the large shifts and extra band multiciplities. This is ruled out by the mass spectrometric observation of nearly pure $^{13}C^{16}O_2$ in the direct-inlet decomposition of the precursor $Ag_2{}^{13}CO_3$ and statements from the supplier that, on the basis of the method of synthesis, the ^{13}C-labeled silver carbonate should not have significant ^{18}O content. The asymmetric C−O stretch at ca. 1200 cm^{-1} also shifts substantially on isotopic substitution (ca. 15−50 cm^{-1}), but the complexity and variation of the band shapes in that spectral area upon isotopic substitution precluded definitive analysis. The symmetric C−O stretch at ca. 985 cm^{-1} showed relatively little shift. Finally, the carbonate out-of-plane bending mode at 818 cm^{-1} for $(Ph_3P)_2Pt(CO_3)$ shifts 25 cm^{-1} to 793 cm^{-1} for the labeled complex.

X-ray Structures. Single-crystal X-ray structural studies have been performed on two different crystalline modifications of (dppp)Pt(CO_3), one with a dichloromethane of solvation and the other without. Selected bond distances and angles are given in Tables 3 and 4. Aside from conformational differences primarily associated with the phenyl groups (see Table S10 of dihedral angles in Supporting Information), the structures are nearly identical. The only significant differences in bond distances and angles involve the center methylene carbon (C3) of the dppp ligand. From Figure 1 (right) it can be seen that in the room-temperature, solvated structure this carbon has rather high displacement amplitudes, leading to shortened bond distances and a larger C2−C3−C4 bond angle due to fitting of the banana-shaped electron-density distribution with an ellipsoidal function. In the low-temperature structure of the unsolvated complex (Figure 1, left), these displacements are lower, yielding more accurate bond distances and angles. In both structures the Pt−dppp six-membered chelate ring adopts a flattened-chair cyclohexane form, as commonly observed.[1] A number of apparent C−H···O and, in the solvated structure, C−H···Cl weak, intra- and intermolecular hydrogen-bonding interactions are observed (H···O < 2.5 Å and H···Cl < 3.2 Å; see Tables S11 and S12 and descriptive information in the Supporting Information). The carbonate ligand bond distances and angles show no statistically significant differences in any of the total of five (LL)Pt(CO_3) complexes that have been

---

(36) Kegley, S. E.; Schaverien, C. J.; Freudenberger, J. H.; Bergman, R. G.; Nolan, S. P.; Hoff, C. D. *J. Am. Chem. Soc.* **1987**, *109*, 6563−6565.

(37) Cf.: Li, J. J. J.; Sharp, P. R. *Inorg. Chem.* **1994**, *33*, 183−184 and references therein.

(38) Massoud, S. S.; Milburn, R. M. *Inorg. Chim. Acta* **1988**, *154*, 115−119.

(39) Woon, T.-C.; O'Connor, J. *Aust. J. Chem.* **1979**, *32*, 1661−1667.

(40) Allen, D. L.; Green, M. L. H.; Bandy, J. A. *J. Chem. Soc., Dalton Trans.* **1990**, 541−549.

(41) Goldsmith, J. A.; Ross, S. D. *Spectrochim. Acta* **1968**, *24A*, 993−998.

(42) Gatehouse, B. M.; Livingstone, S. E.; Nyholm, R. S. *J. Chem. Soc.* **1958**, 3137−3142.

(43) Nakamoto, K.; Fujita, J.; Tanaka, S.; Kobayashi, M. *J. Am. Chem. Soc.* **1957**, *79*, 4904−4908.

(44) Goldsmith, J. A.; Ross, S. D. *Spectrochim. Acta* **1967**, *23A*, 1909−1915.

(45) Greenaway, A. M.; Dasgupta, T. P.; Koshy, K. C.; Sadler, G. G. *Spectrochim. Acta* **1986**, *42A*, 949−954.

(46) Healy, P. C.; White, A. H. *Spectrochim. Acta* **1973**, *29A*, 1191−1195.

(47) Elliott, H.; Hathaway, B. J. *Spectrochim. Acta* **1965**, *21*, 1047−1054.

(48) Fujita, J.; Martell, A. E.; Nakamoto, K. *J. Chem. Phys.* **1962**, *36*, 339−345.

(49) Hester, R. E.; Grossman, W. E. L. *Inorg. Chem.* **1966**, *5*, 1308−1312.

studied by single-crystal X-ray diffraction, namely LL = $(PMe_3)_2$,[24] $(PEt_3)_2$,[23] $(P\text{-}i\text{-}Pr_3)_2$,[22] $(PPh_3)_2$ (two crystalline forms),[50,51] and dppp (the present work), except for the PMe_3 complex, which has a very asymmetric carbonate ligand, possibly due to hydrogen-bonding interactions with the water molecules present.[24]

Conclusions

Platinum carbonate complexes have proven to be useful synthetic intermediates for the preparation of a wide range of Pt^0,[2,52,53] Pt^{II},[1,7,54,55] and even Pt^{IV} complexes.[56] The formation of volatile byproducts, e.g., CO_2 and H_2O, in these reactions makes the isolation of pure products especially easy. The present work provides significantly increased access to these generally air-stable carbonate precursors, the improved silver carbonate route being particularly simple and straightforward in most cases. The carbonate ligand parameters for these complexes, e.g., the ^{13}C NMR chemical shifts, $^{31}P-^{13}C$ and $^{195}Pt-^{13}C$ NMR coupling constants, C=O distances, and C=O stretching frequencies, do not change sufficiently as a function of phosphine to permit systematic correlations with, e.g., phosphine basicity[57] or diol binding constants.[1] Apparently, the electronic effect of the phosphines is not efficiently transmitted to the C=O portion of the carbonate ligand. Phosphine basicity does, however, appear to be linked to the synthetic difficulties we encountered, the greatest problems occurring with the electron-deficient dppm and dfppe carbonate complexes. We believe that this may be due to their higher tendency to undergo decomposition via ligand-induced loss of carbon dioxide to generate reactive platinum oxo species as evidenced by the exchange and phosphine oxidation reactions of $(dppp)Pt(CO_3)$ reported elswhere.[34]

Acknowledgment. We thank Drs. Morris Bullock and Thomas Koetzle for helpful discussions and Nicole Brunkan for some experiments. This research was carried out at Brookhaven National Laboratory under Contract DE-AC02-76CH00016 with the U.S. Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences. The participation of K.S.K. in this work as a Science and Engineering Research Student was supported by the U.S. Department of Energy Office of University and Science Education Programs, Office of Energy Research.

Supporting Information Available: Text giving additional experimental details, infrared spectra, and tables of crystallographic data, atomic coordinates, and bond distances and angles (17 pages). Ordering information is given on any current masthead page.

IC9603159

---

(50) Gregg, M. R.; Powell, J.; Sawyer, J. F. *Acta Crystallogr.* **1988**, *C44*, 43−46.
(51) Cariati, F.; Mason, R.; Robertson, G. B.; Ugo, R. *Chem. Commun.* **1967**, 408.
(52) Blake, D. M.; Leung, L. M. *Inorg. Chem.* **1972**, *11*, 2879−2883.
(53) Blake, D. M.; Mersecchi, R. *J. Chem. Soc. D* **1970**, 1045−1046.
(54) Clarke, D. A.; Kemmitt, R. D. W.; Mazid, M. A.; McKenna, P.; Russell, D. R.; Schilling, M. D.; Sherry, L. J. S. *J. Chem. Soc., Dalton Trans.* **1984**, 1993−2002.
(55) Eaborn, C.; Metham, T. N.; Pidcock, A. *J. Chem. Soc., Dalton Trans.* **1975**, 2212−2214.
(56) Eaborn, C.; Pidcock, A.; Steele, B. R. *J. Chem. Soc., Dalton Trans.* **1975**, 809−813.
(57) Sowa, J. R.; Angelici, R. J. *Inorg. Chem.* **1991**, *30*, 3534−3537 and references therein.