Spectroscopy Measurements. Spectra were recorded on a Bruker WH 90 (17.87 MHz for ^{29}Si) and a Bruker WM 500 (99.27 MHz for ^{29}Si). All samples were 50% solutions in C_6D_6 (10-mm tube). Chemical shifts are given downfield (δ) from Me_4Si as internal standard.

For the SPT spectra, the experiments were performed by using the technique previously describe in the literature.[17] The following parameters were used: time for SPT π pulse = 0.1 s, time for ^{29}Si pulse = 11 μs (α = 90°), and recycle delay = 5 s. The theoretical spectra were calculated on a Leanord Sil Z16 PC and were drawn on a Hewlett-Packard 7475 A digital plotter.

Acknowledgment. We thank MM. B. Barbe and M. Pétraud (Cesamo, University of Bordeaux I) for carrying out the 90-MHz measurements and D. Davoust (University of Paris VI) for the 500-MHz measurements. Special thanks are also due to Dr. T. N. Mitchell of Dortmund University for helpful and valuable discussions.

Registry No. **1**, 754-05-2; **2**, 4964-02-7; **3**, 4964-03-8; **4**, 762-72-1; **5**, 18292-39-2; **6**, 18178-59-1; **7**, 52152-48-4; **8**, 1438-79-5; **9**, 113947-92-5; **10**, 6224-91-5; **11**, 1578-53-6; ^{29}Si, 14304-87-1.

---

[17] Linde, S. A.; Jakobsen, H. J.; Kimber, B. J. *J. Am. Chem. Soc.* **1975**, *97*, 3219.

Synthesis and Structure of $[Pt_2(\eta^5\text{-}C_5Me_5)_2(CO)_2]$. A Convenient Precursor to Pentamethylcyclopentadienyl Chemistry of Platinum

Neil M. Boag[1]

Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, England

Received September 2, 1987

Reaction of $[PtCl_3CO]^-$ with 2 equiv of $C_5Me_5MgCl{\cdot}THF$ affords $Pt_2(\eta^5\text{-}C_5Me_5)_2(CO)_2$ (**1**) in >80% yield. Treatment of $[PtCl_3CO]^-$ with 1 equiv of $C_5Me_5MgCl{\cdot}THF$ yields a mixture of $[PtCl_3CO]^-$, **1**, and $Pt(\eta^5\text{-}C_5Me_5)(CO)Cl$ (**2**), revealing the intermediacy of **2** in the reaction. A single-crystal X-ray structural determination of **1** was undertaken: formula $C_{22}H_{30}O_2Pt_2$; monoclinic, $P2_1/n$, $Z = 4$, $a = 10.428$ (2) Å, $b = 13.995$ (3) Å, $c = 15.143$ (4) Å, $\beta = 100.53$ (2)°; reflections with $I > 3\sigma(I) = 3452$; $R = 0.038$; $R_w = 0.043$. The dimeric structure consists of two staggered $Pt(\eta^5\text{-}C_5Me_5)(CO)$ units connected by a unbridged platinum–platinum bond of 2.636 (1) Å. Variable–temperature ^{13}C NMR spectroscopy was consistent with rapid CO exchange between the two platinum atoms.

Introduction

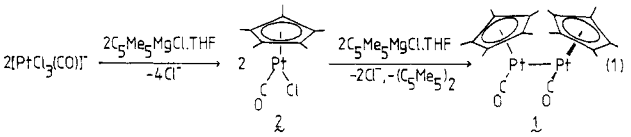
Due to a lack of suitable synthetic routes to the dimeric species $Pt_2(\eta^5\text{-}C_5R_5)_2(CO)_2$, whose analogues in other transition-metal groups provide ready access to an extensive chemistry, cyclopentadienyl chemistry of platinum has been slow to develop.[2]

We have previously described an improved synthesis of $Pt_2(\eta^5\text{-}C_5H_5)_2(CO)_2$ involving formate reduction of $[PtCl_3CO]^-$ to the platinum(I) complex $[Pt_2Cl_4(CO)_2]^{2-}$ followed by metathesis using $(C_5H_5)_2Mg$.[3,4] The modest overall yield from $[PtCl_3CO]^-$ (ca. 35%) and problems associated with elimination reactions of the cyclopentadienyl group on platinum through η^1 intermediates[5] led us to synthesize $Pt_2(\eta^5\text{-}C_5Me_5)_2(CO)_2$ (**1**). In this paper we describe a new high-yield synthetic method to this important starting material.

Results and Discussion

We initially prepared the complex $Pt_2(\eta^5\text{-}C_5Me_5)_2(CO)_2$ (**1**) in 65% overall yield by metathesis of the dianion $[Pt_2Cl_4(CO)_2]^{2-}$ with $C_5Me_5MgCl{\cdot}THF$. This method is, of course, analogous to that used for the synthesis of $Pt_2(\eta^5\text{-}C_5H_5)_2(CO)_2$.[4] However, we have now found that this same complex may be obtained *directly* from the reaction of THF solutions of $[PtCl_3(CO)]^-$ with 2 equiv of $C_5Me_5MgCl{\cdot}THF$ in >80% yields.

Treatment of $[PtCl_3(CO)]^-$ with 1 equiv of $C_5Me_5MgCl{\cdot}THF$ affords some insight into the course of this reduction. IR and NMR analysis of the reaction solution shows it to be a mixture of starting anion, the dimer **1**, and $Pt(\eta^5\text{-}C_5Me_5)(CO)Cl$ (**2**) (see Table I). A second equivalent of the Grignard reagent converts this mixture primarily to $Pt_2(\eta^5\text{-}C_5Me_5)_2(CO)_2$, clearly revealing the intermediacy of **2** in this reaction.[6] After crystallization of the dimer, the σ-coupled byproduct C_5Me_5–C_5Me_5 may be isolated from the residue by sublimation.[7]



A single-crystal X-ray structure determination of **1** revealed it to contain two $Pt(\eta^5\text{-}C_5Me_5)(CO)$ subunits, the two adjacent terminal carbonyl groups being orientated at approximately 105° to each other (Figure 1). The

---

[1] This work was partially undertaken at Syracuse University, Syracuse, NY 13244-1200.

[2] Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds. *Comprehensive Organometallic Chemistry*; Pergamon: Oxford, 1982; Vol. 6, pp 734–736.

[3] This complex was first prepared in 6% yield: Fischer, E. O.; Schuster-Woldan, H.; Bittler, K. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1963**, *18B*, 429.

[4] Boag, N. M.; Goggin, P. L.: Goodfellow, R. J.; Herbert, I. R. *J. Chem. Soc., Dalton Trans.* **1983**, 1101. Boag, N. M.; Goodfellow, R. J.: Green, M.; Hessner, B.; Howard, J. A. K.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1983**, 2585.

[5] Anderson, G. K.; Cross, R. J. *J. Chem. Soc., Chem. Commun.* **1986**, 1502.

[6] Small amounts of a volatile, unstable, yellow platinum complex with a single band in the IR at 2013 cm^{-1} are also produced in this reaction. We have not been able to isolate this material in a pure state for identification.

[7] Jutzi, P.; Kohl, F. *J. Organomet. Chem.* **1979**, *164*, 141.

0276-7333/88/2307-1446$01.50/0 © 1988 American Chemical Society

Table I. Spectroscopic Data for Complexes 1–3

	IR[a] ν_{CO}, cm^{-1}	NMR (ppm)[b] ^1H[c]	NMR (ppm)[b] $^{13}C\{^1H\}$[d]	NMR (ppm)[b] $^{195}Pt\{^1H\}$[e]
[$Pt_2(\eta^5\text{-}C_5Me_5)_2(CO)_2$] (1)	1989, 1968	2.00 (±9.2, ±14.7)	166.8 (CO) (2303)[f] 103.9 (*C*Me) (9, 20) 11.2 (Me)	−1747
[$Pt(\eta^5\text{-}C_5Me_5)(CO)Cl$] (2)	2044	1.94[g] (17.9)	166.4 (CO) (2538) 109.6 (*C*Me) (33) 10.0 (Me)	−25
[$Pt_2(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)(CO)_2$] (3)	2005, 1984	1.89 (Cp*) (±12.4, ±14.5) 5.64 (Cp) (±6.0, ±12.8)		−1513 (PtCp*) −2272 (PtCp) (8983)

[a] In hexane solution. [b] Spectra measured at ambient temperatures; platinum coupling constants (Hz) in parentheses. [c] In C_6D_6 solution at 100 MHz unless otherwise noted. [d] In $CDCl_3$ solution at 75 MHz; TMS, 0.0 ppm. [e] In CH_2Cl_2 solution at 64 MHz; Ξ = 21.4 MHz. [f] $|^1J_{PtC} + {}^2J_{PtC}|$; see text. [g] $CDCl_3$ solution at 300 MHz.

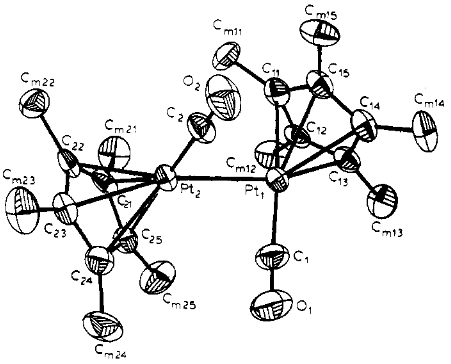


Figure 1. ORTEP drawing of $Pt_2(\eta^5\text{-}C_5Me_5)_2(CO)_2$ (1) with non-hydrogen atoms represented by thermal ellipsoids at the 50% probability level: Pt(1)–Pt(2) = 2.636 (1) Å; Pt(1)–C(1) = 1.83 (1) Å; Pt(2) - C(2) = 1.84 (1) Å; torsion angle C(1)–Pt(1)–Pt-(2)–C(2) = 105.0 (6)°.

carbonyl groups bend over (average angle 79.7°) the platinum–platinum bond whose length of 263.6 pm is at the long end of the range reported for platinum(I) dimers,[8] possibly as a result of steric congestion between the two pentamethylcyclopentadienyl groups. This particular configuration may be adopted to minimize the electronic repulsions of the two adjacent metal-centered full MO's which project above and below the plane defined at each metal center by the carbonyl carbon, the metal, and the center of the C_5Me_5 group.[9] The observed orientation would also allow these MO's to overlap with the π^* orbital of the carbonyl group on the adjacent metal. As judged by the Pt–C–O angle (average 175.5°), this latter interaction is, however, small.

The structure of complex 1 may be contrasted to those found for the nickel and palladium analogues. In these species, the carbonyl groups bridge the two metal centers.[10]

Multinuclear NMR and IR spectroscopic studies of 1 confirmed that the structure found in the solid state is maintained in solution (Table 1) although proton NMR spectra that exhibit resolved coupling to the ^{195}Pt may only be obtained at observing frequencies of 100 MHz and below due to chemical shift anisotropy associated with the ^{195}Pt. Of note is the room-temperature carbon-13 NMR spectrum of a ^{13}CO-enriched sample of 1 which exhibits a 1:8:18:8:1 multiplet for the carbonyl group. At reduced temperatures, the two inner satellite resonances were found to broaden and finally collapse. This is the expected behavior for exchange of terminal carbonyl groups between two platinum atoms. A limiting spectrum was not reached at −90 °C.

Table II. Bond Lengths and Selected Angles for $Pt_2(\eta^5\text{-}C_5Me_5)_2(CO)_2$ (1)

Bond Distances (Å)			
Pt(1)–Pt(2)	2.636 (1)		
Pt(1)–C(1)	1.83 (1)	Pt(2)–C(2)	1.84 (1)
C(1)–O(1)	1.13 (2)	C(2)–O(2)	1.11 (2)
Pt(1)–C(11)	2.33 (1)	Pt(2)–C(21)	2.36 (1)
Pt(1)–C(12)	2.35 (1)	Pt(2)–C(22)	2.33 (1)
Pt(1)–C(13)	2.28 (1)	Pt(2)–C(23)	2.28 (1)
Pt(1)–C(14)	2.35 (1)	Pt(2)–C(24)	2.34 (1)
Pt(1)–C(15)	2.35 (1)	Pt(2)–C(25)	2.29 (1)
Pt(1)–Cg(1)	1.99 (...)[a]	Pt(2)–Cg(2)	1.98 (...)[a]
C(11)–C(12)	1.45 (2)	C(21)–C(22)	1.39 (2)
C(12)–C(13)	1.43 (2)	C(22)–C(23)	1.43 (2)
C(13)–C(14)	1.44 (2)	C(23)–C(24)	1.44 (2)
C(14)–C(15)	1.38 (2)	C(24)–C(25)	1.43 (2)
C(15)–C(11)	1.42 (2)	C(25)–C(21)	1.46 (2)
C(11)–C(m11)	1.52 (2)	C(21)–C(m21)	1.50 (2)
C(12)–C(m12)	1.55 (2)	C(22)–C(m22)	1.52 (2)
C(13)–C(m13)	1.52 (2)	C(23–C(m23)	1.50 (2)
C(14)–C(m14)	1.54 (2)	C(24)–C(m24)	1.52 (2)
C(15)–C(m15)	1.52 (2)	C(25–C(m25)	1.54 (2)
Bond Angles (deg)			
Pt(2)–Pt(1)–C(1)	79.0 (4)	Pt(1)–Pt(2)–C(2)	80.5 (4)
Pt(2)–Pt(1)–Cg(1)	131.0 (...)[a]	Pt(1)–Pt(2)–Cg(2)	131.8 (...)[a]
C(1)–Pt(1)–Cg(1)	149.9 (...)[a]	C(2)–Pt(2)–Cg(2)	147.6 (...)[a]
Pt(1)–C(1)–O(1)	176 (1)	Pt(2)–C(2)–O(2)	175 (1)

[a] The symbols Cg(1) and Cg(2) are used to denote the centers of gravity for the five carbon atoms of the C_5Me_5 ring. They are therefore listed without an estimated standard deviation.

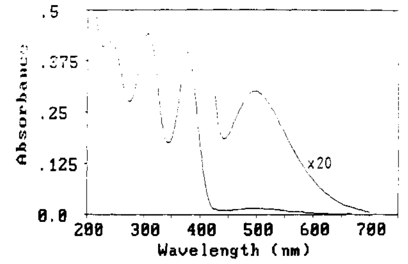


Figure 2. UV–vis spectrum of a 1.4 × 10^{-5} M solution of $Pt_2(\eta^5\text{-}C_5Me_5)_2(CO)_2$ (1) in hexane recorded in a 1-cm cell.

The UV spectrum (Figure 2) of $Pt_2(\eta^5\text{-}C_5Me_5)_2(CO)_2$ compares well to other metal–metal dimers. The absorption at 373 nm is thus assigned to the σ–σ^* transition of the metal–metal bond and the complex exhibits photochemistry associated with cleavage of this bond.[11] For example, photolysis of a mixture of 1 and $Pt_2(\eta^5\text{-}C_5H_5)_2(CO)_2)$ in hexane affords an equilibrium mixture of the

---

(8) Couture, C.; Farrar, D. H.; Fisher, D. S.; Gukathasan, R. R. *Organometallics* **1987**, *6*, 532.

(9) Jemmis, E. D.; Pinhas, A. R.; Hoffmann, R. *J. Am. Chem. Soc.* **1980**, *102*, 2576.

(10) Mise, T.; Yamazaki, H. *J. Organomet. Chem.* **1979**, *164*, 391. Byers, L. R.; Dahl, L. F. *Inorg. Chem.* **1980**, *19*, 680. Jack, T. R.; May, C. J.; Powell, J. *J. Am. Chem. Soc.* **1977**, *99*, 4707. Boag, N. M.; Boucher, D.; Davies, J. A.; Miller, R. W.; Pinkerton, A. A.; Syed, R. *Organometallics* **1988**, *7*, 791.

(11) Meyer, T. J.; Casper, J. V. *Chem. Rev.* **1985**, *85*, 187.

starting materials and the mixed dimer $Pt_2(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)(CO)_2$ (**3**) identified by NMR and IR spectroscopies.[12]

The development of a high-yield synthetic route to $Pt_2(\eta^5\text{-}C_5Me_5)_2(CO)_2$ has enabled us to successfully exploit the mononuclear chemistry associated with the $Pt(\eta^5\text{-}C_5Me_5)(CO)$ fragment. It has also provided an entry into platinum clusters. We will shortly report our results in these areas.

Experimental Section

All manipulations were undertaken in an atmosphere of dinitrogen by using standard Schlenk techniques. Solvents were freshly distilled from sodium/potassium alloy (hexane) or sodium/benzophenone (THF). The complexes $[Pt_2Cl_4(CO)_2][NBu_4]_2$, $[PtCl_3(CO)][NBu_4]$, $[PtCl_3(^{13}CO)][NPr_4]$[3] and $C_5Me_5MgCl{\cdot}THF$[13] were prepared by using literature methods. The Grignard reagent was used as a solution in THF and standardized by titration of a hydrolyzed aliquot with acid. NMR spectra were obtained on either a Varian XL100 or a Bruker AC300. IR spectra were recorded on a Perkin-Elmer 1710 FTIR or an IBM IR/32 spectrometer.

Preparation of $Pt_2(\eta^5\text{-}C_5Me_5)_2(CO)_2$ (1). (a) From $[Pt_2Cl_4(CO)_2][NBu_4]_2$. To 1.3 mL of a 0.43 M solution of $C_5Me_5MgCl{\cdot}THF$ (0.56 mmol) in THF was added finely powdered $[Pt_2Cl_4(CO)_2][NBu_4]_2$ (300 mg, 0.28 mmol). The slurry was stirred for 15 min during which time it turned a dark red. All volatiles were removed in vacuo, and the residue was extracted with 3 × 20 mL of hexane. The combined hexane solutions were filtered and reduced in vacuo. Crystallization at −20 °C afforded dark crystals of $Pt_2(\eta^5\text{-}C_5Me_5)_2(CO)_2$ (**1**) (145 mg, 72%).

(b) From $[PtCl_3(CO)][NBu_4]$. To $[PtCl_3(CO)][NBu_4]$ (5.90 g, 10.3 mmol) partially dissolved in THF (50 mL) was added dropwise with stirring 47 ml of a 0.44 M THF solution of $C_5Me_5MgCl{\cdot}THF$ (20.7 mmol) over 10 min. The solution was stirred for 1 h, and all volatiles were removed in vacuo. The residue was extracted with 3 × 150 ml of warm (35 °C) hexane, filtered and the volume reduced to *ca* 300 ml. Crystallization at −20 °C afforded 2.305 g of dark crystals. The supernatant was reduced to ca. 30 mL and recooled, affording a further 0.76 g of product. The supernatant liquid of the second recrystallization was stripped to dryness in vacuo, and a water-cooled sublimation probe was inserted into the reaction vessel. The residue was heated at 65 °C at 0.1 mmHg pressure overnight, and a mass of white crystals together with a small amount of a pale yellow oil were collected on the probe (vide infra). The residue from the sublimation was disolved in hexane (5 mL), filtered, and cooled to afford a third crop of the product **1** (0.120 g). The total yield was 3.185 g (86%). Anal. Calcd for $C_{22}H_{30}O_2Pt_2$: C, 36.87; H, 4.22. Found: C, 36.93; H, 4.42.

The pale yellow oil that exhibited a single carbonyl band at 2013 cm^{-1} in hexane could not be isolated in a pure state. A pure sample of the white crystals was obtained by washing the sublimate off the probe with ether, allowing the solution to evaporate, and leaving the residue exposed to air for a few days. Subsequent sublimation of this residue (40 °C, 0.1 mmHg) afforded white crystals of $C_5Me_5\text{–}C_5Me_5$. NMR: ^1H (C_6D_6, 300 MHz) 1.76 (s, 12 H), 1.67 (s, 12 H), 1.15 (s, 6 H) ppm;[7] $^{13}C\{^1H\}$ ($CDCl_3$, 75 MHz) 141.8, 133.2, 59.8, 19.3, 12.5, 10.9 ppm.

Cophotolysis of $Pt_2(\eta^5\text{-}C_5Me_5)_2(CO)_2$ and $Pt_2(\eta^5\text{-}C_5H_5)_2(CO)_2$. A mixture of $Pt_2(\eta^5\text{-}C_5Me_5)_2(CO)_2$ (14 mg) and $Pt_2(\eta^5\text{-}C_5H_5)_2(CO)_2$ (10 mg) were dissolved in hexane (5 mL) and photolyzed by using unfiltered radiation from a 450-W medium pressure Hanovia lamp. Infrared spectra were recorded every 30 min. Bands at 2005 and 1984 cm^{-1} attributable to $Pt_2(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)(CO)_2$ grew in, reaching a maximum after 90 min. Further photolysis resulted in the decay of these bands and the bands due to $Pt_2(\eta^5\text{-}C_5H_5)_2(CO)_2$. After several hours, the solution only exhibited absorptions due to $Pt_2(\eta^5\text{-}C_5Me_5)_2(CO)_2$. The complex $Pt_2(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)(CO)_2$ was identified spectroscopically (Table II).

Table III. Crystal and Intensity Collection Data for $Pt_2(\eta^5\text{-}C_5Me_5)_2(CO)_2$ (1)

fw	716.7
temp, °C	20 ± 1
space group	monoclinic, $P2_1/n$
a, Å	10.428 (2)
b, Å	13.995 (3)
c, Å	15.143 (4)
β, deg	100.53 (2)
V, Å^3	2172.8 (8)
Z	4
ρ(calcd), g cm^{-3}	2.190
cryst dimens, mm	0.40 × 0.52 × 0.56
radiatn	Mo Kα
abs coeff, cm^{-1}	130.1
transmissn factors	0.261–1.000
scan type	ω
2θ ranges, deg/scan rates, deg min^{-1}	3.0–43.0/6.0; 43.0–55.0/3.0
total measd data	4997
unique data used ($I > 3\sigma(I)$)	3452
total no. of variables	236
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.038
$R_w = [\sum w(\|F_o\| - \|F_c\|)^2/\sum w\|F_o\|^2]^{1/2}$	0.043

Table IV. Fractional Atomic Coordinates for $Pt_2(\eta^5\text{-}C_5Me_5)_2(CO)_2$ (1)[a]

atom	x	y	z	$10B$,[b] Å^2
Pt(1)	0.0395 (1)	0.1686 (1)	0.2002 (1)	26 (1)
Pt(2)	0.0407 (1)	0.1757 (1)	0.3742 (1)	24 (1)
O(1)	−0.1653 (11)	0.0273 (8)	0.2149 (7)	66 (4)
O(2)	0.2748 (10)	0.0575 (7)	0.3782 (7)	51 (3)
C(1)	−0.0898 (14)	0.0836 (9)	0.2102 (9)	41 (4)
C(2)	0.1890 (12)	0.1048 (7)	0.3748 (8)	31 (3)
C(11)	0.1855 (13)	0.2917 (8)	0.1876 (8)	32 (3)
C(12)	0.0714 (11)	0.3070 (8)	0.1187 (7)	30 (3)
C(13)	0.0566 (12)	0.2250 (8)	0.0616 (8)	32 (3)
C(14)	0.1696 (12)	0.1652 (8)	0.0890 (8)	35 (3)
C(15)	0.2437 (12)	0.2052 (8)	0.1648 (8)	32 (3)
C(21)	−0.0511 (10)	0.3205 (7)	0.4128 (7)	27 (3)
C(22)	0.0176 (12)	0.2789 (7)	0.4910 (8)	28 (3)
C(23)	−0.0344 (12)	0.1875 (8)	0.5063 (7)	32 (3)
C(24)	−0.1475 (12)	0.1733 (8)	0.4374 (8)	35 (3)
C(25)	−0.1525 (12)	0.2521 (8)	0.3765 (8)	32 (3)
C(m11)	0.2392 (15)	0.3627 (9)	0.2609 (8)	42 (4)
C(m12)	−0.0224 (14)	0.3935 (9)	0.1069 (10)	46 (4)
C(m13)	−0.0438 (15)	0.2145 (11)	−0.0240 (8)	48 (4)
C(m14)	0.2023 (16)	0.0753 (9)	0.0390 (10)	48 (5)
C(m15)	0.3742 (12)	0.1684 (9)	0.2136 (9)	44 (4)
C(m21)	−0.0338 (15)	0.4186 (8)	0.3761 (9)	44 (4)
C(m22)	0.1308 (13)	0.3256 (8)	0.5541 (8)	39 (3)
C(m23)	0.0024 (17)	0.1230 (9)	0.5855 (9)	49 (5)
C(m24)	−0.2468 (16)	0.0927 (9)	0.4322 (11)	55 (5)
C(m25)	−0.2630 (15)	0.2703 (11)	0.2964 (10)	53 (5)

[a] The numbers of parentheses are the estimated standard deviations in the last significant digit. [b] Equivalent isotropic thermal parameter. This is one-third the trace of the orthogonalized B_{ij} tensor.

Crystal Structure Determination.[14] Purple parallelepipeds of $Pt_2(\eta^5\text{-}C_5Me_5)_2(CO)_2$ (**1**) were grown from hexane at −20 °C. The crystals were mounted on the end of a glass fiber and crystallographic data was obtained on a Nicolet four-circle autodiffractometer equipped with a graphite monochromator. The unit cell dimensions were obtained from 15 reflections having $2\theta > 20°$. During the collection of the intensity data, six check reflections were monitored after every 300 measurements. There was no significant variation of these reflections during the data collection (Table III).

The intensity data were corrected empirically for absorption effects by using psi scans for seven reflections having 2θ between 8.1° and 35.1° and were then reduced to relative squared am-

---

[12] This reaction takes place in the absence of light, but only over several days. The dimer **1** also slowly reacts with CCl_4 in the dark to form **2** in 50% yield as evinced by proton NMR spectroscopy.

[13] Fagan, P. J.; Manriquez, J. M.; Maatta, E. A.; Seyam, A. M.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 6650.

[14] The crystal structure determination was undertaken by the Crystalytics Company, P.O. Box 82286, Lincoln, NB 68501.

plitudes, $|F_o|^2$, by means of standard Lorentz and polarization corrections. A correction was also made for the effects of anomalous dispersion associated with the platinum atoms.[15]

The coordinates of the platinum atoms were determined by using heavy-atom Patterson techniques on the 1935 reflections having $I > 3\sigma(I)$ obtained from the 2θ range 3.0–43.0°. The remaining 22 carbon and two oxygen atoms were subsequently located from difference maps (Table IV). The hydrogen atoms were not located. All the atoms were refined with anisotropic thermal parameters, and correction was made for isotropic extinction. During the final cycles of refinement, 3452 reflections having $I > 3\sigma(I)$ obtained from the 2θ range 3.0–55.0° were employed.

The top four peaks in the final difference Fourier (1.66–1.36 e/Å^3) were within 0.86 Å of the Pt atoms. There were no other peaks in the final difference Fourier above the noise level (1.00 e/Å^3).

All calculations were performed on a Data General Eclipse S-200 computer with 64K of 16-bit words, a parallel floating-point processor for 32- and 64-bit arithmetic and a Data General disk with 10-million 16-bit words using versions of the Nicolet (Syntex) E-XTL or SHELXTL interaction crystallographic software package as modified at the Crystalytics Co.

Acknowledgment. This work was supported in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No. 1, 113792-89-5; 3, 113779-30-9; $[Pt_2Cl_4(CO)_2][NBu_4]_2$, 89554-12-1; $C_5Me_5MgCl\cdot THF$, 107495-40-9; $[PtCl_3(CO)][NBu_4]$, 34964-16-4; $Pt_2(\eta^5\text{-}C_5H_5)_2(CO)_2$, 76680-94-9.

Supplementary Material Available: Tables of crystal data, atomic coordinates, anisotropic thermal parameters, bond lengths, bond angles, and torsion angles (16 pages). A listing of structure factor amplitudes (15 pages). Ordering information is given on any current masthead page.

---

[15] *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, pp 149–150.

Communications

Photochemical Formation of a Metal–Metal Bond Following Outer-Sphere Intervalence Excitation in the Ion Pair $[Co^I(CO)_3(PPh_3)_2][Co^{-I}(CO)_4]$

Arnd Vogler* and Horst Kunkely

Institut für Anorganische Chemie, Universität Regensburg
Universitätsstr. 31, D-8400 Regensburg, FRG

Received November 25, 1987

Summary: The absorption spectrum of the ion pair $[Co^I(CO)_3(PPh_3)_2][Co^{-I}(CO)_4]$ in acetone displays a long-wavelength band at λ_{max} = 386 nm that is assigned to an intervalence transfer (IT) transition from Co^{-I} to Co^{+I}. Upon IT excitation a photoreaction occurs according to the equation $[Co^I(CO)_3(PPh_3)_2][Co^{-I}(CO)_4] \rightarrow [(PPh_3)(CO)_3Co^0\text{–}Co^0(CO)_3PPh_3] + CO$ with a quantum yield of $\Phi = 0.012$. It is suggested that in the primary photochemical step the radicals $[Co(CO)_3(PPh_3)_2]$ and $[Co(CO)_4]$ are generated. These radicals are labile and undergo dissociation and substitution reactions and finally dimerize to yield the stable photoproduct.

An important photoreaction of dimeric carbonyl complexes is the homolytic splitting of the metal–metal bonds.[1] McCullen and Brown[2] and then Tyler and co-workers have shown that in the presence of suitable ligands (L) this primary photochemical step is followed by a disproportionation:[3]

$$(OC)_nM\text{–}M(CO)_n \xrightarrow{h\nu} 2\cdot M(CO)_n$$

$$2\cdot M(CO)_n + L \rightarrow [M^{+I}(CO)_nL]^+[M^{-I}(CO)_n]^-$$

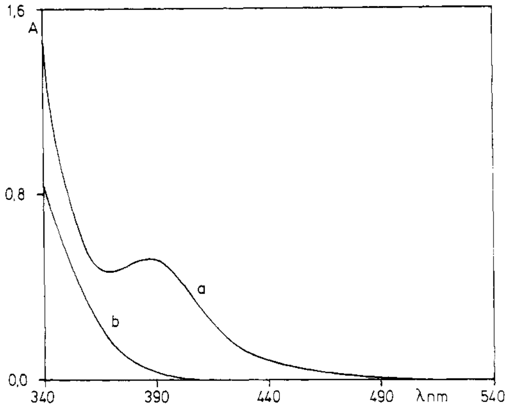


Figure 1. Electronic absorption spectra of 1.94×10^{-4} M $[Co(CO)_3(PPh_3)_2][Co(CO)_4]$ (a) and 1.90×10^{-4} M $[Co(CO)_3(PPh_3)_2][BPh_4]$ (b) in acetone under argon (298 K, 1-cm cell).

The starting complex $M_2(CO)_{2n}$ and the ion pair $[M^I(CO)_nL]^+[M^{-I}(CO)_n]^-$ may be considered as alternate forms of metal–metal interaction. In the dinuclear complex this interaction leads to the appearance of a $\sigma\sigma^*$ (M–M) band

---

[1] Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic: New York, 1979.

[2] McCullen, S. B.; Brown, T. L. *Inorg. Chem.* 1981, *20*, 3528.

[3] (a) Stiegman, A. E.; Stieglitz, M.; Tyler, D. R. *J. Am. Chem. Soc.* 1983, *105*, 6032. (b) Goldman, A. S.; Tyler, D. R. *J. Am. Chem. Soc.* 1984, *106*, 4066. (c) Stiegman, A. E.; Tyler, D. R. *Coord. Chem. Rev.* 1985, *63*, 217. (d) Stiegman, A. E.; Goldman, A. S.; Philbin, C. E.; Tyler, D. R. *Inorg. Chem.* 1986, *25*, 2976. (e) Philbin, C. E.; Goldman, A. S.; Tyler, D. R. *Inorg. Chem.* 1986, *25*, 4434. (f) Goldman, A. S.; Tyler, D. R. *Inorg. Chem.* 1987, *26*, 253.

0276-7333/88/2307-1449$01.50/0