Reactivity of the "$Pt_2(\mu_2\text{-}S)$" Unit in Dimeric Platinum Complexes

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Received August 24, 1988

Reaction of the complex $Pt_3(\mu\text{-}CO)_3(P^tBu_2Ph)_3$ (1) with an atmosphere of hydrogen sulfide or a stoichiometric quantity of elemental sulfur results in the formation of $Pt_2(\mu\text{-}S)(CO)_2(P^tBu_2Ph)_2$ (4). Treatment of complex 4 with 2 equiv of methyl iodide initially gives a cation, $[Pt_2(\mu\text{-}SCH_3)(CO)_2(P^tBu_2Ph)_2]^+$ (6), which proceeds on to the final product $Pt_2I_2(CO)_2(P^tBu_2Ph)_2$ (5) in quantitative yields with elimination of dimethyl sulfide. Two equivalents of *m*-chloroperbenzoic acid effect the oxidation of the sulfide ligand in 4 yielding the complex $Pt_2(\mu\text{-}SO_2)(CO)_2(P^tBu_2Ph)_2$ (2). A symmetric dimeric Pt complex, believed to be the bridged sulfoxide $Pt_2(\mu\text{-}SO)(CO)_2(P^tBu_2Ph)_2$ (7), has been observed as a reaction intermediate. Abstraction of the SO_2 ligand from complex 2 using trimethylamine *N*-oxide results in aggregation to form the starting material 1 and $Pt_3(\mu\text{-}SO_2)(\mu\text{-}CO)_2(P^tBu_2Ph)_3$ (3) in approximately a 1:3 ratio. Complex 3 does not react with Me_3NO but does react with CO to give mixtures of 1 and 2. Complete regeneration of 1 was achieved by the reaction of 2 and Me_3NO under a CO atmosphere.

Introduction

Transition-metal complexes of sulfur-containing molecules have traditionally been studied as models for the activation of their oxo analogues or the development of desulfurisation catalysts and for use in the synthesis of organosulfur compounds. There has been considerable success in the synthesis of these complexes, in particular the sulfide ligand has proven to be quite versatile both in the variety of reagents that have been used for its incorporation into complexes[1-3] and in its bonding geometry in metal cluster compounds. The polynuclear coordination to platinum has been established directly from crystallographic studies[4,5] and illustrates the strong Lewis basicity of the sulfide ligand. It is not surprising therefore to find evidence of its susceptibility to electrophilic attack in protonation and alkylation reactions. An excellent example of this behavior is found[6] in the bridging sulfide ligand of the dimeric complex $Pt_2(\mu\text{-}S)_2(PPh_3)_4$, the nucleophilicity of which is so strong that it readily undergoes alkylation at the sulfur atom with both chloroform and dichloromethane. The reaction chemistry of sulfur dioxide and transition metals also is attracting attention because of the diversity of possible modes of bonding of SO_2 to metal centers. In polynuclear complexes, the SO_2 ligand always is found bridging metal centers.

In this investigation we report the reactivity of the "μ-S" unit in dimeric platinum(I) complexes. Previous work[1] involving the chemistry of the triangular platinum cluster $Pt_3(\mu\text{-}CO)_3(P^tBu_2Ph)_3$ (1) has shown that exposure of a solution of 1 to an atmosphere of sulfur dioxide results in quantitative formation of $Pt_2(\mu\text{-}SO_2)(CO)_2(P^tBu_2Ph)_2$ (2). Allowing a solution of 2 to stand for several days results in an aggregation process in which the dimer is initially converted to a mixture of the trimeric products $Pt_3(\mu\text{-}SO_2)(\mu\text{-}CO)_2(P^tBu_2Ph)_3$ (3) and $Pt_3(\mu\text{-}CO)(\mu\text{-}SO_2)_2(P^tBu_2Ph)_3$. Complex 2 may be quantitatively regenerated from this mixture by exposure to an atmosphere of CO.[1] The synthesis of 2 and the subsequent aggregation were also observed in the reaction of the μ-SO_2 analogue of 1, $Pt_3(\mu\text{-}SO_2)_3(P^tBu_2Ph)_3$,[7] with an atmosphere of CO.

During the course of this work, Mingos and Hallam[8] reported that the reaction of $Pt_3(\mu\text{-}SO_2)_3(PCy_3)_3$ with CO led to the immediate formation of the PCy_3 analogue of 3, $Pt_3(\mu\text{-}CO)_2(\mu\text{-}SO_2)(PCy_3)_3$, and a small amount of the $Pt_2(\mu\text{-}SO_2)(CO)_2(PCy_3)_2$ dimer. Although PCy_3 is known to be slightly more basic than P^tBu_2Ph,[9] we believe that the observed difference in behavior between the PCy_3 and P^tBu_2Ph systems arises from the different steric demands[10] of the phosphine ligands.

The Pt dimer $Pt_2(\mu\text{-}S)(CO)_2(P^tBu_2Ph)_2$ (4) has been previously obtained from reaction of 1 with carbonyl sulfide.[1] Addition of 1.5 equiv of elemental iodine to a solution of 1 yields $Pt_2I_2(CO)_2(P^tBu_2Ph)_2$ (5) quantitatively.[11] The halogen ligands in this complex are thought to be terminally bound in orthogonally displaced square-planar configurations about the Pt centers based upon the structure obtained from an X-ray crystal study of the chloro analogue $Pt_2Cl_2(CO)_2(P^tBu_2Ph)_2$.[12]

The three dimeric Pt species 2, 4, and 5 possess the same framework which consists of two platinum centers coupled by a metal-metal bond with terminally bound trans phosphine ligands and terminally bound carbonyl ligands. It is therefore of interest to investigate the interconversion amongst these complexes by reactions at the ligand centers.

Experimental Section

All reactions were carried out under an N_2, CO, or Ar atmosphere. The solvents were dried by using standard techniques under N_2 and were degassed by the freeze-evacuation method.

All NMR spectra were recorded on a Varian XL-200 spectrometer operating at 200 (^1H) and 81 MHz (^{31}P). ^1H NMR

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0276-7333/89/2308-0813$01.50/0

Table I. ^{31}P NMR and IR Spectroscopic Data for Complexes 1–7

complex	δ^a	^1J(P–Pt),^{b} Hz	^2J(P–Pt), Hz	^3J(P–P), Hz	IR (ν_{CO}),^{c} cm^{-1}
1	86.3	4826	419	48	1768, 1830
2	59.3	3957	318	76	2001, 2040
3	84.1 (d)	4442	394	48	1811, 1865
	104.2 (t)	4972	475	48	
4	71.7	3169	107	128	1968, 2008
5	77.4	2786	219	161	2017, 2039
6I^-	70.9	3144	8	111	*d*
6$[BF_4]^-$	70.3	3117	10	110	2036, 2070
7	66.6	3357	115	107	*d*

^{a} Relative to H_3PO_4. ^{b} P refers to ^{31}P and Pt refers to ^{195}Pt. ^{c} In CH_2Cl_2. ^{d} Species only observed in NMR experiment.

chemical shifts were measured relative to TMS. External $P(OMe)_3$ in C_6D_6 or $CO(CD_3)_2$ was used as reference in the measurement of $^{31}P\{^1H\}$ NMR spectra, but chemical shifts are reported herein with reference to 85% H_3PO_4. Infrared spectra of the complexes were recorded on a Nicolet 5DX FTIR spectrometer. Microanalyses were performed by Analytische Laboratorien, West Germany.

$Pt(COD)_2$,[13] $Pt(P^tBu_2Ph)(C_2H_4)_2$,[13] $Pt_3(\mu\text{-}CO)_3(P^tBu_2Ph)_3$ (**1**),[14] $Pt_2(\mu\text{-}SO_2)(CO)_2(P^tBu_2Ph)_2$ (**2**),[1] and $Pt_2(\mu\text{-}S)(CO)_2(P^tBu_2Ph)_2$ (**4**)[1] were prepared by the referenced literature methods. All products were characterized by ^{31}P NMR and IR spectroscopy unless otherwise stated. These data are given in Table I.

Preparation of $Pt_2I_2(CO)_2(P^tBu_2Ph)_2$ (5).[11] I_2 (0.029 g, 1.14 × 10^{-4} mol) was added to a CH_2Cl_2 solution (10 mL) of **1** (0.100 g, 7.48 × 10^{-5} mol). After the solution was stirred for 5 min, the solvent was removed under reduced pressure and the residue was recrystallized from hexanes/ether mixtures giving an orange-brown solid in 80% yield. Analytically pure samples of **5** could not be obtained as the compound decomposes on standing in solution. Complex **5** reacts with 1 equiv of I_2 giving $PtI_2(CO)(P^tBu_2Ph)$ in quantitative yields. Anal. Calcd for $PtI_2(CO)(P^tBu_2Ph)$: C, 34.9; H, 4.5. Found: C, 34.8; H, 4.5.

Reaction of 1 with H_2S. A CH_2Cl_2 solution (20 mL) of **1** (0.050 g, 3.74 × 10^{-5} mol) was exposed to an atmosphere of H_2S for 3 days. The solvent volume was reduced under vacuum to approximately 5 mL. The solution was filtered, and the remainder of the solvent was removed to yield **4** in 70% yield.

Reaction of 1 with S_8. Elemental sulfur (0.004 g, 1.5 × 10^{-5} mol) was added to a CH_2Cl_2 (10 mL) solution of **1** (0.100 g, 7.48 × 10^{-5} mol) and stirred (24 h). Filtration, followed by solvent removal under reduced pressure, gave **4** in 60% yield.

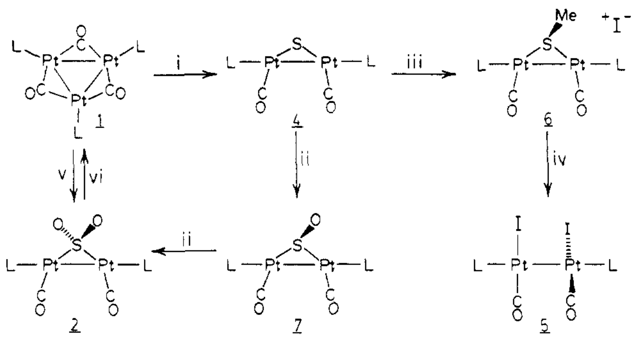
Reaction of 4 with 2 Equiv of CH_3I. A 0.130 M solution of CH_3I was prepared by the volumetric dilution of CH_3I (0.460 g, 3.24 × 10^{-3} mol) in CH_2Cl_2 (25.00 mL). The solution of **4** (0.060 g, 6.5 × 10^{-5} mol) in CH_2Cl_2 (5 mL) was stirred for 45 min following the addition of 1.00 mL of the CH_3I solution. Solvent removal under reduced pressure gave the orange-brown product **5** in 95% yield.

It was later found that **5** is sufficiently stable in CH_3I to permit the reaction to be carried out with neat CH_3I as the solvent.

Synthesis of $[Pt_2(\mu\text{-}SCH_3)(CO)_2(P^tBu_2Ph)_2]^+[BF_4]^-$ (6[BF_4]$^-$). $[Me_3O][BF_4]$ (0.012 g, 8.11 × 10^{-5} mol) was added to **4** (0.075 g, 8.13 × 10^{-5} mol) in CH_2Cl_2 (20 mL). The solution was stirred for 20 min. The solvent was removed under reduced pressure to give the orange-yellow product in quantitative yield. Anal. Calcd for $Pt_2(SCH_3)(CO)_2(P^tBu_2Ph)_2BF_4$: C, 36.3; H, 4.8. Found: C, 36.1; H, 4.7. ^{1}H NMR data: ^{t}Bu, δ = 1.17 ppm (d, 36 H), $|^3J(^{31}P-^1H)|$ = 16 Hz; Ph, $\delta \approx$ 7.3 ppm (m, 10 H); SCH_3, δ = 1.96 ppm (t of t, 3 H), $|^3J(^{195}Pt-^1H)|$ = 22 Hz, $|^4J(^{31}P-^1H)|$ = 22 Hz.

Reaction of 4 with 2 Equiv of MCPBA. *m*-Chloroperbenzoic acid (MCPBA) (0.038 g, 2.2 × 10^{-4} mol) was added to a CH_2Cl_2 (20 mL) solution of **4** (0.100 g, 1.08 × 10^{-4} mol). The solution was stirred (30 min) and then filtered after reduction of the solvent volume to approximately 5 mL. Removal of the remainder of the solvent under reduced pressure followed by recrystallization from CH_2Cl_2/EtOH gave **2** in 75% yield.

Scheme I^a



^{a} (i) OCS, H_2S or S_8; (ii) MCPBA; (iii) CH_3I; (iv) CH_3I – $(CH_3)_2S$; (v) SO_2; (vi) $(CH_3)_3NO$ + CO.

Attempt To Isolate $Pt_2(\mu\text{-}SO)(CO)_2(P^tBu_2Ph)_2$ (7) via Reaction of 4 with 1 Equiv of MCPBA. *m*-Chloroperbenzoic acid (0.019 g, 1.1 × 10^{-4} mol) was added to a CH_2Cl_2 (20 mL) solution of **4** (0.100 g, 1.08 × 10^{-4} mol) which was stirred for 10 min. A ^{31}P NMR spectrum of the reaction mixture after reduction of solvent volume revealed the presence of a 1:1 ratio of **4** and **2**.

Reaction of 2 with $Pt(P^tBu_2Ph)(C_2H_4)_2$. A mixture of $Pt(P^tBu_2Ph)(C_2H_4)_2$ (0.028 g, 5.92 × 10^{-5} mol) and $Pt_2(\mu\text{-}SO_2)(CO)_2(P^tBu_2Ph)_2$ (0.056 g, 5.86 × 10^{-5} mol) were dissolved in a minimum volume of CH_2Cl_2. Solvent removal under reduced pressure after 20 min gave the yellow solid $Pt_3(\mu\text{-}SO_2)(\mu\text{-}CO)_2(P^tBu_2Ph)_3$[1] (**3**) in 90% yield.

Reactions of 2 with Me_3NO. For both the N_2 and CO atmospheres, freshly sublimed Me_3NO (0.079 g, 1.05 × 10^{-3} mol) was added to a CH_2Cl_2 solution (10 mL) of **2** (0.100 g, 1.05 × 10^{-4} mol) which was then stirred for 3 h under the appropriate atmosphere. ^{31}P NMR spectroscopy revealed the presence of **3** and **1** under N_2, and exclusively **1** under CO, in the reaction mixtures.

Results and Discussion

The results of this investigation into the chemistry of dimeric Pt complexes are summarized in Scheme I. The ^{31}P NMR and IR spectroscopic data for complexes are listed in Table I. Since our initial preparation[1] of **4** via exposure of a CH_2Cl_2 solution of **1** to carbonyl sulfide, other routes to its formation have been found. Addition of 1 equiv of elemental sulfur to a CH_2Cl_2 solution of **1** produces **4** in approximately 60% yield. The product may also be obtained, in approximately 70% yield, using hydrogen sulfide as a reagent. In both cases, the reduced yield results from decomposition during reaction giving phosphine sulfide and an insoluble solid assumed to be Pt metal and/or PtS based upon the absence of IR peaks corresponding to carbonyl group stretches. The phosphine sulfide was characterized by agreement of the ^{31}P NMR spectrum of an authentic sample[15] with the anomalous singlet observed in the reaction mixture. The use of H_2S as reagent in the formation of **4** is thought to result in the formation of dihydrogen as a byproduct. This is supported by the absence of extraneous signals in the ^{1}H NMR spectrum of the reaction mixture and by the quantitative recovery of H_2 as the byproduct of the related reaction of hydrogen sulfide with $Pd_2X_2(\mu\text{-dppm})_2$[3] (X = Cl, Br, I).

Quantitative conversion of **4** into **5** was effected by the addition of 2 equiv of methyl iodide to a CH_2Cl_2 solution of **4**. Complete reaction requires approximately 45 min. Characterization of dimethyl sulfide as the reaction byproduct was achieved by comparison of the ^{1}H NMR spectrum of an authentic sample with that of the reaction mixture. While analytically pure samples of **5** could not be obtained, ^{31}P NMR spectroscopy indicates that **5** is the

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same Pt complex obtained from the reaction of 1 and 1.33 equiv of I_2.[11] Comparison of the spectroscopic data for complex 5, presented in Table I, with the data[12] for the complex $Pt_2Cl_2(CO)_2(P^tBu_2Ph)_2$, strongly suggests that the two dimers are isostructural. The complex $Pt_2Cl_2(CO)_2(Pt^tBu_2Ph)_2$, prepared by the reaction of 1 and 1.33 equiv of Cl_2, has been characterized by single-crystal X-ray diffraction.[12] The proposed structure for 5, based upon that of $Pt_2Cl_2(CO)_2(P^tBu_2Ph)_2$, is given is Scheme I. Complex 5 reacts with 1 equiv of I_2 resulting in quantitative formation of $PtI_2(CO)(P^tBu_2Ph)$, for which analytical data has been obtained. Monitoring the reaction of 4 with 2 equiv of methyl iodide, by ^{31}P NMR spectroscopy, revealed the presence of a symmetric dimeric Pt-based intermediate, shown in Scheme I. The concentration of the intermediate dimer reached a maximum approximately halfway through the time required for full conversion to 5. Consideration of the symmetry of the intermediate and the Lewis base nature of the sulfido ligand[6,16] suggests that the intermediate arises from methylation of the S atom to yield the corresponding $[Pt_2(\mu\text{-}SCH_3)(CO)_2(P^tBu_2Ph)_2]^+$ complex 6, where the iodide ion acts as the anion. All attempts to isolate the cation 6 from this reaction were unsuccessful. The reaction of 4 with 1 equiv of MeI generates 1:1 mixtures of 4 and 5.

The proposed structure of the cationic intermediate is supported by its synthesis as a stable $[BF_4]^-$ salt from the reaction of 4 with 1 equivalent of $[Me_3O][BF_4]$ (see the ^{31}P NMR data of the I^- and $[BF_4]^-$ salts in Table I). The symmetry of the dimer is also evident in the ^1H NMR spectrum of the $[BF_4]^-$ salt as the $\mu\text{-}SCH_3$ proton signal exhibits the expected $^1H\text{-}^{195}Pt\text{-}^{31}P$ triplet of triplets coupling pattern. The formation of 6 represents a logical first step in the conversion of 4 into 5 with the formation of dimethyl sulfide as the byproduct. The instability of 6 in solution in comparison to that of the $[BF_4]^-$ salt may be explained in terms of subsequent insertion of the iodide anion into the coordination sphere of one of the Pt centers which is not possible in the case of the $[BF_4]^-$ anion. A slow rate of insertion would account for the buildup of 6 that permits its detection. Fast reaction of this species with the second equivalent of methyl iodide yields the two required products. This mechanism is supported by the absence of reaction of the $[BF_4]^-$ salt of $[Pt_2(\mu\text{-}SCH_3)(CO)_2(P^tBu_2Ph)_2]^+$ with 1 equiv of $[Me_3O][BF_4]$ which suggests that the conversion of 4 to 5 does not proceed via a dimethylated bridging sulfide species.

The oxidation chemistry of the bridging sulfide ligand of 4 was investigated in an attempt to effect its conversion into 2. Following the work of Balch et al.[2] and Rauchfuss et al.[17] preparation of 2 was achieved in good yield (>80%) by the addition of 2 equiv of the oxidant *m*-chloroperbenzoic acid, MCPBA, to solutions of 4. The stepwise nature of the process is evident in the ^{31}P NMR spectrum of the reaction mixture. The presence of a symmetric Pt dimer, in addition to 4 and 2, represents strong evidence of the existence of the sulfoxide analogue 7 as an intermediate in the conversion of the sulfido to the sulfur dioxide dimer. This would arise from the reaction of 4 with the first equivalent of MCPBA. Attempts to synthesize 7 via reaction of 4 with 1 equiv of MCPBA yields essentially a 1:1 mixture of 4 and 2, with only traces of the desired product. A variety of oxidants were tested in attempts to isolate the sulfoxide dimer 7. Complex 4 was found to be stable to reaction with atmospheric oxygen,[1] trimethylamine *N*-oxide and sodium periodate, while the use of 30% aqueous hydrogen peroxide results in the decomposition of the complex.

The inability to isolate 7 is in contrast to the work of James et al. in which controlled stepwise oxidation of the bridging sulfide ligand of $Pd_2(\mu\text{-}S)(\mu\text{-}dppm)_2X_2$[3] (X = Cl, Br, I), leading to the clean formation of the sulfoxide analogue, was achieved by using a stoichiometric addition of MCPBA. The use of excess aqueous H_2O_2 also generated the sulfoxide species with no further oxygen incorporation.

The reaction of 2 with a 10-fold excess of Me_3NO requires several minutes to go to completion. A ^{31}P NMR spectrum of the reaction mixture after 1 h indicates the presence of $Pt_3(\mu\text{-}SO_2)(\mu\text{-}CO)_2(P^tBu_2Ph)_3$ (3) in approximately 75% abundance and 1 in approximately 25% abundance. The appearance of these products is accompanied by the formation of a colorless viscous oil. The reaction is thought to proceed via net abstraction of SO_2 from 2 by the Me_3NO to generate two L–Pt–CO fragments in situ which are then capable of two possible competing steps, the relative magnitudes of which depend upon the extent of reaction. Those generated early in the course of reaction are present in a large excess of 2, and the species may therefore react with 2 to yield 3. This is consistent with the formation of 3 from reaction of 2 with the "$Pt(P^tBu_2Ph)$" fragment. ^{31}P NMR spectroscopy revealed that 3 is exclusively formed when $Pt(C_2H_4)_2(P^tBu_2Ph)$ is added to a solution of 2. As the reaction of 2 and Me_3NO approaches completion, the local concentrations of liberated L–Pt–CO species in solution reach the point where aggregation of the fragments generates 1.

Characterization of the isomeric form of the byproduct is important in ascertaining by which of two possible mechanisms Me_3NO abstraction of SO_2 from 2 takes place. Formation of an $SO_2{\cdot}Me_3NO$ adduct involving a N–O–S linkage (I) is possible from interaction of the Me_3NO oxygen atom with the sulfur center of the coordinated SO_2. This isomer is reported[18,19] to be the product of the reaction of Me_3NO with free SO_2. The alternate mechanism would involve initial oxygen transfer from Me_3NO to the coordinated SO_2 to yield NMe_3 and bridging SO_3. Adduct formation may then occur between these species via a N–S linkage (II) to yield $Me_3N{\cdot}SO_3$ as has been observed in the reaction of Me_3N with free SO_3.[18]

$$\underset{\text{I}}{(CH_3)_3N\text{-}O\text{-}SO_2} \qquad \underset{\text{II}}{(CH_3)_3N\text{-}SO_3}$$

The heating of the Me_3NOSO_2 adduct (I), prepared by the literature method,[19] above its melting point results in a rearrangement of the adduct and formation of a clear, viscous oil.[20,21] Comparison of the IR spectra of the adduct and its decomposition product with that of the clear, viscous oil byproduct formed in the reaction of 2 and Me_3NO reveals that the byproduct consists predominantly of the adduct with some of its decomposition product. It is proposed that, on the basis of these similar physical and spectroscopic properties, the reaction oil represents the products of the Me_3NOSO_2 adduct and that sulfur dioxide abstraction occurs via direct reaction with the amine oxide. The absence of reaction between Me_3NOSO_2 and 1 after 2 days demonstrates that the formation of the oil occurs during the process of sulfur dioxide abstraction rather than

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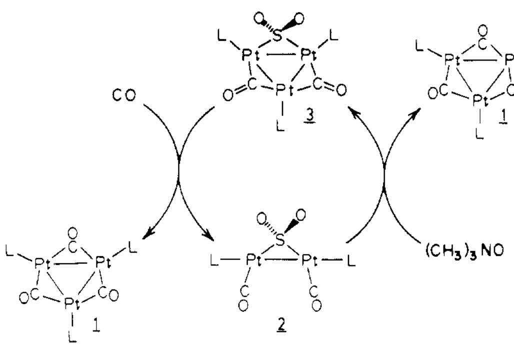
Scheme II



the rearrangement occurring at platinum centes subsequent to the formation of the Me_3NOSO_2 adduct.

A route by which either **2** or **3** may be converted to **1** is shown in Scheme II. Addition of Me_3NO to a solution of **2** under an atmosphere of CO leads to the regeneration of **1**. Addition of Me_3NO to **2** yields the previously discussed mixture of **1** and **3**, while the presence of the CO atmosphere converts **3** back to **2** and more **1**. In this manner, the cycle is repeated until complete conversion of **2** or **3** to **1** has been affected. The absence of reaction between **3** and a 10-fold excess of Me_3NO under N_2 after 4 days indicates that abstraction of SO_2 from the system occurs exclusively from **2**. This lies in contrast to the work of Mingos and Hallam,[8] who reported the conversion of $Pt_3(\mu\text{-}CO)_2(\mu\text{-}SO_2)(PCy_3)_3$ to the PCy_3 analogue of **1**, in high yield, using Me_3NO.

Acknowledgment. We thank the Natural Sciences and Engineering Council of Canada for operating and equipment grants.

Registry No. **1**, 62931-81-1; **2**, 97703-27-0; **3**, 97719-79-4; **4**, 97689-48-0; **5**, 118714-49-1; **6**[I], 118714-50-4; **6**[BF_4], 118714-52-6; **7**, 118722-42-2; MCPBA, 937-14-4; Pt(P-*t*-Bu_2Ph)(C_2H_4)$_2$, 79503-49-4; PtI_2(CO)(P-*t*-Bu_2Ph), 19618-88-3; Me_3NO, 1184-78-7; S^{2-}, 18496-25-8.

Synthetic and X-ray Structural Studies on Pentabenzylcyclopentadienyl Derivatives of Manganese, Rhenium, and Iron

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Received August 31, 1988

(η^5-Pentabenzylcyclopentadienyl)tricarbonylmanganese (**3**) and -rhenium (**4**) have been prepared in low yields from reactions between pentabenzylcyclopentadiene and dimanganese or dirhenium decacarbonyl in refluxing aromatic solvents. A reaction between pentabenzylcyclopentadienyllithium and anhydrous iron(II) chloride has afforded decabenzylferrocene (**5**) in 34% yield. The mixed-ring metallocenes pentamethylpentabenzylferrocene (**6**) and 1,2,3,4,5-pentabenzylferrocene (**7**) have been obtained via reactions of (C_5R_5)Fe(acac) (R = Me, Bz; acac = acetylacetonate) intermediates. The crystal structures of **3** and **5** have been determined via single-crystal X-ray diffraction. (η^5-C_5Bz_5)Mn(CO)$_3$ crystallizes in the monoclinic space group $P2_1/n$ with a = 12.908 (4) Å, b = 14.907 (3), Å, c = 18.575 (8) Å, β = 108.21 (4)°, and D_{calcd} = 1.28 g cm^{-3} for Z = 4. The manganese center is pseudotetrahedral with Mn–C(η^5) = 2.14 (1) Å, Mn–Cent = 1.77 Å, and Mn–CO = 1.772 (6) Å. (η^5-C_5Bz_5)$_2$Fe·2$C_6H_5CH_3$ crystallizes in the monoclinic space group $P2_1/c$ with a = 13.871 (6) Å, b = 22.135 (8) Å, c = 23.700 (9) Å, β = 103.47 (5)°, and D_{calcd} = 1.19 g cm^{-3} for Z = 4. The substituted cyclopentadienyl rings are parallel (Cent–Fe–Cent = 179.6°) and are staggered. The average Fe–C and Fe–Cent distances are 2.058 (7) and 1.65 Å, respectively. In **3**, four of the phenyl rings are oriented up and away from the manganese center, with the fifth down toward the tripod ligands. Unexpectedly, in **5** all five phenyl rings in each ligand are oriented away from the metal center.

Introduction

The η^5-pentamethylcyclopentadienyl ligand has played an extremely significant role in organometallic chemistry during the past 20 years, due to both steric and electronic influences imparted by the methyl substituents on the corresponding (η^5-pentamethylcyclopentadienyl)metal compounds. More recently, studies on related η^5-pentaphenyl- and η^5-pentabenzylcyclopentadienyl derivatives of metals have been undertaken.[1–4] The η^5-C_5Bz_5 (Bz = benzyl) ligand is of special interest, since a variety of conformational features and shielding effects can be expected for organometallic compounds that contain this very bulky organic moiety.

We have recently described the first η^5-pentabenzylcyclopentadienyl derivatives of the transition metals,

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