Reactions of Trisulfonated Triphenylphosphine, TPPTS, with Cobalt Carbonyls in Water

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The synthesis and characterization of a series of water-soluble cobalt carbonyl complexes is described: HCo-$(CO)_3(TPPTS)$, $HCo(CO)_2(TPPTS)_2$, and $[Co(CO)_3(TPPTS)]^-$, where TPPTS = $P(m\text{-}C_6H_4SO_3Na)_3$. Investigation of the substitution of $Co_2(CO)_8$ by TPPTS shows that the reaction proceeds via the ionic intermediate $[Co(CO)_3$-$(TPPTS)_2][Co(CO)_4]$, which is relatively stable in water. The hydride complexes are stable in the presence of water at low pH. Under these conditions, it is likely that the sodium cations are replaced with protons. A variety of reaction pathways to these compounds are described. The dimer, $Co_2(CO)_6(TPPTS)_2$, undergoes base-induced disproportionation above pH 10 to yield the substituted anion $[Co(CO)_3(TPPTS)]^-$ as the only carbonyl-containing product. In the course of this investigation, crystals of the sodium salt of $Co_2(CO)_6(TPPTS)_2$ were obtained. Crystal data: space group $C2/c$, $a = 31.723(16)$ Å, $b = 11.244(14)$ Å, $c = 41.267(14)$ Å, $\beta = 107.456(35)°$, $Z = 8$. Data were collected at 193 K, and a total of 5898 reflections with $I > 3\sigma(I)$ were collected. The sodium ions and solvent are partially disordered, and two of the sulfonate groups are disordered. This and two very long cell axes contribute to the final residuals, $R = 0.0858$ and $R_w = 0.0997$. Qualitative aspects of the structure are discussed.

The use of trisulfonated triphenylphosphine (TPPTS) for the development of water-soluble homogeneous catalysts has attracted a great deal of attention in recent years.[1-6] Further development of water-soluble transition metal catalysts requires that the coordination chemistry of TPPTS and other water-soluble phosphines to be thoroughly investigated.[7]

Notably, a wide variety of coordination compounds with TPPTS as a ligand have been reported by Herrmann et al.[1] It is apparent from these syntheses that the range of compounds to be prepared from TPPTS will closely follow those available with its nonsulfonated analog, PPh$_3$. One important difference between TPPTS and PPh$_3$ is that the former is very susceptible to oxidation. As much as 15–30% of TPPTS is lost to the oxide during its synthesis;[2,3] also, oxidation is a common side reaction in some syntheses which use TPPTS. Patin et al. have shown, for example, that Rh(III) catalytically oxidizes TPPTS in the presence of water.[4]

Aqueous-phase hydroformylation catalysts which utilize TPPTS are based on $HRh(CO)(TPPTS)_3$, as reported by Kuntz.[2a] More recently, Fache and Basset prepared water-soluble ruthenium hydrogenation catalysts with TPPTS,[5] and the cobalt carbonyl derivative $Co_2(CO)_6(TPPTS)_2$ has been used in the aqueous phase for olefin hydroformylation.[6] It also has been reported that the reductive carbonylation of Co(II) in the presence of TPPTS yields $HCo(CO)(TPPTS)_3$.[1] Structural information on metal TPPTS complexes first became available with the single-crystal structure determination of $[Na\text{-}Crypt]_3\{W(CO)_5[P(C_6H_4SO_3)_3]\}$.[8]

In related chemistry, many complexes of the monosulfonated analog of TPPTS have been reported. Thus Wilkinson et al. have prepared $HRh(CO)[PPh_2(m\text{-}C_6H_4SO_3Na)]_3$[9] as a hydroformylation catalyst; Joo et al. have used ruthenium complexes of $PPh_2(m\text{-}C_6H_4SO_3Na)$ for hydrogenation;[10] and the palladium compound $Pd[PPh_2(m\text{-}C_6H_4SO_3Na)]_3$ has been used by Casalnuovo for cross-coupling reactions.[11]

Recently we reported the preparation of a new series of sulfonated phosphines, $P[(CH_2)_x\text{-}p\text{-}C_6H_4SO_3Na]_3$ ($x = 1, 2, 3, 6$), and their nickel carbonyl and palladium chloride complexes, $Ni(CO)_{4-n}\{P[(CH_2)_x\text{-}p\text{-}C_6H_4SO_3Na]_3\}_n$ ($n = 1, 2$) and *trans*-$\{P[(CH_2)_x\text{-}p\text{-}C_6H_4SO_3Na]_3\}_2PdCl_2$.[12] The new sulfonated phosphines are sterically and electronically similar to their nonsulfonated analogs.[12]

Here we describe the reactions of $Co_2(CO)_8$ and other cobalt carbonyl compounds with TPPTS as monitored by IR and NMR spectroscopy. The chemistry includes the formation of $[Co(CO)_3$-$(TPPTS)_2][Co(CO)_4]$ (1) and $Co_2(CO)_6(TPPTS)_2$ (2), the base-induced disproportionation of 2, and the formation of the TPPTS-substituted cobalt carbonyl anion and hydride. In the course of this investigation, we attempted to determine the X-ray structure of 2. The structure is complicated by disorder among some of the sulfonate groups, sodium cations, and solvent. Qualitatively the structure provides a simple model for the adsorbed layer present in supported aqueous-phase catalysts based on TPPTS transition metal complexes.[13]

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Experimental Section

All reactions and measurements were carried out using standard Schlenk techniques under an atmosphere of purified argon or CO. Toluene, pentane, and diethyl ether were distilled from sodium benzophenone ketyl. In-house-deionized water and methanol and acetone from Fisher Scientific were deoxygenated by distillation under argon prior to use. Hydrochloric acid (36%) was received from Fisher Scientific and used as supplied. $Co_2(CO)_8$, Na metal, and Hg were purchased from Aldrich. $HCo(CO)_4$[14] and $Na[Co(CO)_4]$[15] were synthesized according to known procedures. TPPTS was prepared by sulfonation of PPh_3 with fuming sulfuric acid (20% SO_3).[3] All NMR solvents and standards (D_2O, THF-d_8, and TMS) were obtained from Cambridge Isotope Laboratories. The water-soluble chemical shift NMR standard sodium 3-(trimethylsilyl)tetradeuteriopropionate (TSP) was received from Wilmad Glass Co. Routine NMR measurements were done on a Bruker WP 200 at observation frequencies of 200.133 MHz for ¹H, 50.323 MHz for ¹³C, and 81.015 MHz for ³¹P. Some high-field ¹H, ¹³C, and ³¹P NMR data were obtained on a Varian RU400 NMR spectrometer at 399.052, 100.577, and 161.903 MHz, respectively. Key to NMR data: s, singlet; d, doublet; t, triplet; dt, doublet of triplet; m, multiplet; br., broad; *, pseudo. Carbon atoms in the phosphine are numbered from the phosphorus atom with the α-carbon labeled (1)C through the γ SO_3Na-attached carbon (3)C. Key to IR data: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder. Infrared spectra were recorded on a Nicolet 5DXB FTIR in matched 0.1-mm solution cells with Irtran windows. Elemental analyses were performed by Atlantic Microlab, Inc.

Synthesis of $Co_2(CO)_6(TPPTS)_2$, (2). Preparation of the dimer was achieved by a modification of previously published procedures.[1,6] TPPTS, 1.14 g (2.00 mmol), was dissolved in 4 mL of water to give a colorless solution. A 4-mL toluene solution containing 0.38 g (1.10 mmol) of $Co_2(CO)_8$ was added to the TPPTS solution. The immiscible phases were vigorously stirred for 1 day under Ar, during which time the aqueous phase became deep brown. The reaction mixture was then extracted three times with pentane in 10-mL portions. The combined organic extracts yielded unreacted $Co_2(CO)_8$. The water layer was dried under vacuum to yield a red-brown solid. This was redissolved in ca. 2 mL of H_2O; the solution was then filtered, and the filtrate was frozen at −78 °C. The frozen solution was layered with 20 mL of methanol, and the mixture was allowed to warm slowly to room temperature. Over 2–3 days, red-brown needle-shaped crystals of $Co_2(CO)_6(TPPTS)_2 \cdot nH_2O \cdot mCH_3OH$ formed. The approximate values of n and m as determined by ¹H NMR spectroscopy are 4 and 2, respectively. Yield: 1.3 g (82%). X-ray crystallography also shows the presence of water and methanol with an apparent stoichiometry of approximately 3.7 H_2O to 1.3 CH_3-OH. The analysis is complicated by disorder among the water and methanol molecules (vide infra).

¹H NMR δ (D_2O): 7.61–7.92 (br m), 7.93–8.10 (s*), 24H, 6 × C_6H_4. ¹³C NMR δ (D_2O): 137.88 (d, J_{PC} = 30.5 Hz, (1)C), 138.37 (d, J_{PC} = 5.7 Hz, (2)C), 146.12 (d, J_{PC} = 6.0 Hz, (3)C), 131.02 (s, (4)C), 132.39 (d, J_{PC} = 13.7 Hz, (5)C), 132.45 (d, J_{PC} = 21.4 Hz, (6)C), 36C, 6 × C_6H_4, 204.40 (t, J_{PC} = 9.2 Hz), 6 × CO. ³¹P NMR δ (D_2O): 68.90 (s). IR ν_{CO} (D_2O): 2017.2 (vw), 1963.3 (vs) cm⁻¹.

Synthesis of $Na[Co(CO)_3TPPTS]$ (3). A Schlenk flask was charged with 0.38 g (2.00 mmol) of $Na[Co(CO)_4]$ and 1.14 g (2.00 mmol) of TPPTS in 10 mL of H_2O at room temperature. The tetracarbonylcobaltate slowly dissolved to give a yellow solution. The reaction mixture was heated to 60 °C under argon and periodically vented to remove evolved CO. When the IR spectrum of the reaction mixture no longer showed evidence of $[Co(CO)_4]^-$, typically 3 days, the reaction mixture was filtered to give a lemon yellow solution. The volume was reduced under vacuum to ca. 1 mL, and 15 mL acetone was added. The product, $Na[(Co(CO)_3(TPPTS)]$, precipitated as a light yellow finely crystalline solid. This was collected by filtration and vacuum-dried. Yield: 1.31 g (89%).

¹H NMR δ (D_2O): 7.47–7.74 (br m), 7.74–7.95 (br d*), 7.95–8.12 (br d*), 12H, 3 × C_6H_4. ¹³C NMR δ (D_2O): 143.37 (d, J_{PC} = 27.5 Hz, (1)C), 137.85 (d, J_{PC} = 9.7 Hz, (2)C), 145.19 (d, J_{PC} = 9.2 Hz, (3)C), 128.78 (s, (4)C), 131.91 (d, J_{PC} = 21.5 Hz, (5)C), 132.00 (d, J_{PC} = 34.6 Hz, (6)C), 18C, 3 × C_6H_4, 212.00 (br s), 3C, 3 × CO. ³¹P NMR δ (D_2O): 62.76 (br s). IR ν_{CO} (H_2O): 1944.5 (w), 1863.7 (vs) cm⁻¹. Anal. Calcd for $C_{21}H_{18}CoNa_4O_{15}PS_3$ ($Na[Co(CO)_3(TPPTS)] \cdot 3H_2O$): C, 32.95; H, 2.37; Co, 7.70; P, 4.05. Found: C, 32.98; H, 2.29; Co, 7.64; P, 4.11.

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Table I. X-ray Crystallographic Data Collection and Refinement Parameters

formula	$C_{43.3}Co_2H_{37.1}Na_{5.5}O_{29}P_2S_6$	space group	$C2/c$ (No. 15)
fw	1540.9	T (K)	193
a (Å)	31.723(16)	radiation (λ Å))	Mo Kα (0.710 73 Å)
b (Å)	11.244(14)	ρ_{calc} (g/cm³)	1.46
c (Å)	41.267(14)	R	0.0856[a]
β (deg)	107.456(35)	R_w	0.0997[b]
V (Å³)	14042(20)	μ, cm⁻¹	7.95
Z	8		

[a] $R = \sum \|F_o\| - |F_c\| / \sum |F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w(|F_o|^2)]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

In Situ Synthesis of $HCo(CO)_3[TPPTS(H)]$ (4). In a typical reaction, 0.076 g (0.10 mmol) of $Na[Co(CO)_3(TPPTS)]$ was placed in a Schlenk vessel and suspended in 2 mL of THF-d_8 at 0 °C. During the addition of 0.05 mL of 36% HCl (~1 mmol), the yellow suspension was converted to a green solution and a white precipitate of NaCl was formed. The reaction mixture was then warmed to room temperature. After ca. 10 min, $HCo(CO)_3[TPPTS(H)]$ could be identified by IR and NMR spectroscopy. In about 1–2 h, a red-brown aqueous phase formed at the bottom of the vessel, which contained $Co_2(CO)_6[(TPPTS(H)]_2$. All attempts to isolate the hydride yielded a mixture of $[Co(CO)_3(TPPTS)_2]^+$ and $Co_2(CO)_6(TPPTS)_2$.

¹H NMR δ (THF-d_8, 5% D_2O): −11.22 (d, J_{PH} = 46.2 Hz), H–Co, 7.51–7.58 (dt*, $J*_{PH}$ = 8.0 Hz), 7.65–7.75 (t*, $J*_{PH}$ = 9.6 Hz), 7.86–7.92 (d*, $J*_{PH}$ = 7.6 Hz), 12H, 3 × C_6H_4. ¹³C NMR δ (THF-d_8, 5% D_2O): 134.97 (d, J_{PC} = 44.2 Hz, (1)C), 135.79 (d, J_{PC} = 17.5 Hz, (2)C), 146.38 (d, J_{PC} = 8.4 Hz, (3)C), 129.43 (s, (4)C), 130.21 (d, J_{PC} = 7.6 Hz, (5)C), 129.93 (d, J_{PC} = 12.2 Hz, (6)C), 18C, 3 × C_6H_4, 200.45 (d, J_{PC} = 45.0 Hz), 3C, 3 × CO. ³¹P NMR δ (THF-d_8, 5% D_2O): 60.20 (s). IR ν_{CO} (THF-d_8, 5% H_2O): 2052.7 (m), 1979.5 (vs) cm⁻¹.

Synthesis of $HCo(CO)_2[TPPTS(H)]_2$ (5). In a typical preparation, 0.25 g (0.50 mmol) of TPPTS(H) was placed in a three-neck flask equipped with a dropping funnel and a gas adapter. The phosphine was dissolved in 1 mL of H_2O, and Ar was bubbled through the solution during the reaction. A hexane solution of 0.25 mmol of $HCo(CO)_4$ (0.2 mol/L) was added dropwise over 1 h to the water phase at 0 °C. After the addition of $HCo(CO)_4$, the reaction mixture was stirred $^1/_2$ h at room temperature, and then washed twice with 10 mL of hexane. The product, $HCo(CO)_2$-$[TPPTS(H)]_2$, remained in the water phase and was isolated as a yellow solid by precipitation with acetone (yield 84%). The disubstituted hydride was identified by NMR and IR spectroscopy.

¹H NMR δ (D_2O): −11.24 (t, J_{PH} = 36.2 Hz), H–Co, 7.46 (br s), 7.85 (br s), 24H, 6 × C_6H_4. ¹³C NMR δ (D_2O): 137.19 (t, J_{PC} = 20.2 Hz, (1)C), 135.65 (t, J_{PC} = 6.9 Hz, (2)C), 142.94 (t, J_{PC} = 4.6 Hz, (3)C), 127.07 (s, (4)C), 129.50 (t, J_{PC} = 4.6 Hz, (5)C), 129.27 (t, J_{PC} = 6.9 Hz, (6)C), 18C, 3 × C_6H_4, 208.71 (br s), 3C, 3 × CO. ³¹P NMR δ (D_2O): 57.10 (br s). IR ν_{CO} (D_2O): 1999.6 (s, 1984.6 sh), 1944.5 (vs, 1925.8 sh) cm⁻¹.

Crystal Structure Determination of $Co_2(CO)_6\{P(m-C_6H_4SO_3)_3\}_2Na_{5.5}$-$(H_3O)_{0.5}(H_2O)_{3.2}(MeOH)_{1.3}$. A very dark red-brown cut crystal of approximate dimensions 0.5 × 0.5 × 0.5 mm³ was mounted on a glass fiber using epoxy cement and placed immediately in the cold N_2 stream (193 K) on the diffractometer. The data were collected on a Rigaku AFC5S fully automated four-circle X-ray diffractometer using Mo Kα (λ = 0.7107 Å) radiation. Data collection parameters are given in Table I. Unit cell parameters were based on 23 reflections in the range 6.8° < 2θ < 11.9°. Peak profiles for those peaks used in the unit cell determination were single with full widths at half-height in the range 0.240–0.275°. Two of the cell axes are very long and necessitated data collection using ω scans. Data were corrected for Lorentz and polarization effects. Crystal and instrument stabilities were checked by measuring three standard reflections after every 150 reflections. Only random variations in intensity were observed, and no correction for decay was made. The analytic form of the scattering factors for the appropriate neutral atoms were corrected for both the real ($\Delta f'$ and imaginary ($\Delta f''$) components of anomalous dispersion.[16] Because of problems encountered in structure solution and refinement, data were collected on three separate crystals. It was concluded that problems with the structure were primarily due to overlap because of the long cell axes and that further attempts were unlikely to yield improvements in the structure. The data reported here are for the third of those attempts. The long cell axes also prevented

(16) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. 4, pp 99–101, 149–150.

the use of ψ-scan data for the absorption correction because of overlap problems in certain orientations of the ψ-scan reflections; consequently, the program DIFABS was used to correct the data for absorption.[17]

The structure was solved using the direct methods routine of SHELXS-86,[18] which located the Co and P atoms. The other manipulations were carried out using the TEXSAN 5.0 structure analysis package.[19] Successive electron density difference maps were used to locate the remaining non-hydrogen atoms. During this process, it became evident that two of the sulfonate groups had a 3-fold rotational disorder of the oxygen atoms. It was possible to refine one of these groups normally (oxygens on S(11)) with independent positional and thermal parameters, but for the other (oxygens on S(23)) it was necessary to constrain the oxygens into a rigid group. For S(11), the two positions refined to occupancies of 0.72/0.28 when the displacement parameters were held fixed at the average value of the isotropic displacement parameters for the nondisordered oxygen atoms. A similar treatment of the O(3) groups for S(23) resulted in occupancies of 0.67/0.33. After this refinement, the occupancies were held constant and the thermal parameters were refined. Because of this disorder problem, the oxygen atoms attached to S(11) could only be refined isotropically. The O(3) groups attached to S(23) were refined as a group but with individual thermal parameters for each atom.

Disorder problems were also encountered in the Na atom positions. Six Na atoms positions are expected on the basis of the formulation of the sulfonated ligand, and five were found and refined without difficulty. The sixth position was more problematic, and it was ultimately realized that a sixth site was present very close to but not exactly lying on a crystallographic inversion center. Assignment of the this position as Na with 0.5 occupancy allowed refinement with displacement parameters and oxygen to Na⁺ distances similar to that observed for the other Na⁺ ions. Further examination of the difference maps showed that the two highest peaks which could have been assigned as Na⁺ would not refine properly and coordination environments were not reasonable for Na⁺. Our current speculation is that the additional charge balance is maintained by the presence of some hydronium ion.

The crystallization of the compound from a mixed H₂O/MeOH solvent system also presents crystallographic complications, as apparently both solvents are present in the crystal lattice coordinated to the Na⁺ ions. The carbon atom (C(1)) of one MeOH molecule was found at unit occupancy and refined normally. A second position near O(3), was refined at partial occupancy (0.3), indicating a H₂O–MeOH substitutional disorder. Several of the residual peaks were also in locations which could indicate other MeOH–H₂O partial substitutions, but the data set was inadequate to allow refinement of the these positions. The exact composition of the solvent molecules present is, therefore, uncertain.

All non-hydrogen atoms were refined anisotropically except for the oxygen atoms attached to S(11) and S(23) as described above, C(1), C(3), C(12A), and C(22C). Anisotropic refinement of the last two was attempted, but the displacement parameters became non-positive definite. Hydrogen atoms on the phenyl rings were included in calculated positions but not refined.

Overall, the complications which arise due to the various types of positional and occupational disorder as well as the peak overlap problems arising from the long cell axes contribute to the higher than desired final residuals. In spite of these problems, there is little question about the chemical correctness of the structure, which agrees well with other compounds in this class.

Results and Discussion

An outline of the observed chemistry of TPPTS with cobalt carbonyls is shown in Scheme I. The synthesis of Co₂(CO)₆-(TPPTS)₂ (2) proceeds via the ionic complex [Co(CO)₃(TPPTS)₂]-[Co(CO)₄] (1). Such ionic intermediates are well-known in the substitution chemistry of cobalt carbonyls in nonaqueous solvents.[20]

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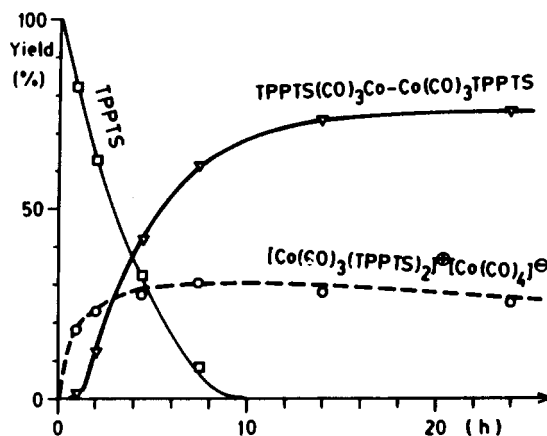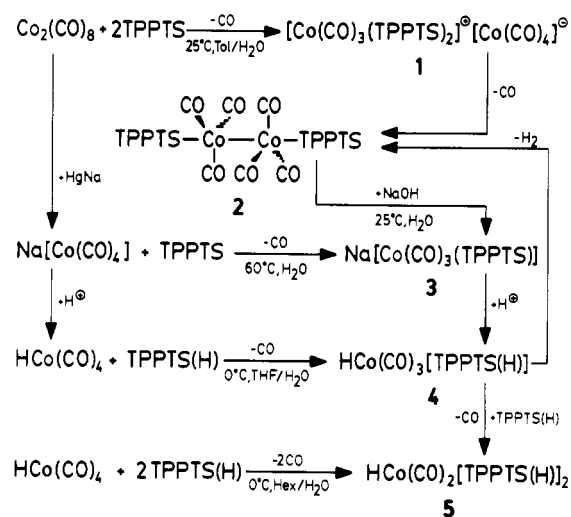

Figure 1. Relative concentration of water-soluble species during the reaction of TPPTS with Co₂(CO)₈ in a two-phase reaction mixture (toluene/water).

Scheme I

The reaction of Co₂(CO)₈ and TPPTS is carried out in a biphasic reaction under CO with Co₂(CO)₈ in toluene and TPPTS in H₂O. When the reaction is followed by ³¹P NMR spectroscopy, it appears that complexes 1 (δ = 57.58 ppm) and 2 (δ = 68.90 ppm) exist in equilibrium in the water phase. The relative concentrations of water-soluble species (TPPTS-oxide as an internal standard) as a function of time are presented in Figure 1. The complete coordination of TPPTS to a cobalt center is reached in about 10 h. The ionic cobalt compound, 1, is the first product, from which the covalent disubstituted cobalt dimer, 2, is formed by loss of CO. Also, infrared spectroscopy confirms the presence of both 1 and 2 in the water phase (ν CO: 2025.4 (w), 2013.0 (w), 1911.7 (vs), 1960.9 (s) cm⁻¹). The anion band is always present in reaction solutions before workup; however, when the crude product is redissolved in water, the 1911.7-cm⁻¹ band indicative of [Co(CO)₄]⁻ is no longer present. All efforts to isolate the ionic compound, 1, yielded 2. Some decomposition occurs with heating, and the overall isolated yield of Co₂(CO)₆-(TPPTS)₂ is approximately 80%.

The phosphine-induced disproportion of Co₂(CO)₈ to yield [Co-(CO)₃L₂][Co(CO)₄] is well-known. Disproportionation is favored by more basic phosphines, while reaction with arsines yields the substituted dimers Co₂(CO)₇L and Co₂(CO)₆L₂ directly in a stepwise fashion.[20] The disproportionation products are generally thermally unstable although the isolation of the P(nBu)₃ analogs has been reported.[21]

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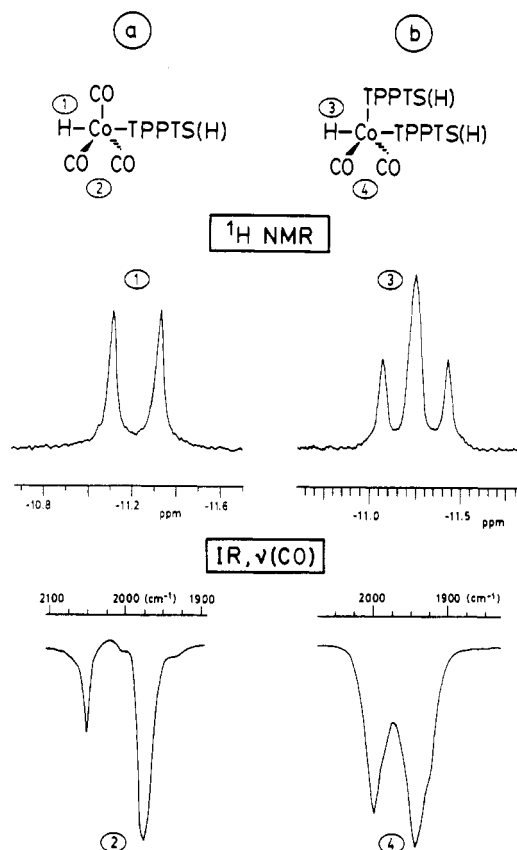
Figure 2. Selected spectra for the hydride complexes $HCo(CO)_3[TPPTS-(H)]$ and $HCo(CO)_2[TPPTS(H)]_2$. Data for the monosubstituted complex was obtained on samples prepared in situ.

Figure 3. Rendering of the structure of the complex anion in **2**, $[Co_2(CO)_6\{P(m\text{-}C_6H_4SO_3)_3\}_2]^{6-}$, as determined by X-ray crystallography.

The base-induced disproportionation of metal carbonyls is one of the cornerstone reactions which defines metal carbonyl chemistry.[22] This type of reaction has not been previously investigated for water-soluble phosphine-substituted cobalt carbonyls. Interestingly, aqueous solutions of $Co_2(CO)_6(TPPTS)_2$ rapidly disproportionate above pH 10 to yield the phosphine-substituted anion $[Co(CO)_3(TPPTS)]^-$, which is identified as the only carbonyl-containing product by IR spectroscopy. (The substituted anion can also be prepared directly from $[Co(CO)_4]^-$; vide infra). Evidence for the expected cobalt(II) aquo complex however has not been obtained. Cleavage of phosphine-substituted cobalt carbonyl complexes in nonaqueous solvents typically is achieved with sodium amalgam without disproportionation. The equivalent reaction with **2**, of course, is not possible in water.

Direct substitution of $Na[Co(CO)_4]$ by TPPTS occurs very slowly at room temperature. Over a period of 3 days, aqueous solutions of the tetracarbonylcobaltate in the presence of TPPTS yield $Na[Co(CO)_3(TPPTS)]$ (**3**). Until recently, $[Co(CO)_4]^-$ had been regarded as inert to substitution;[23] Ungváry and Wojcicki have reported the direct substitution of $[Co(CO)_4]^-$ with some phosphines.[24] For example, $Na[Co(CO)_4]$ reacts slowly with PPh_3 over a period of several days in refluxing THF with an argon purge to yield $[Co(CO)_3(PPh_3)]^-$.[24] The reaction of TPPTS with $Na[Co(CO)_4]$ in water requires 2–3 days at 60 °C. When solid **3** is treated with aqueous THF (ca. 5% water) which contains HCl, the cobalt anion reacts to yield the hydride and a precipitate of NaCl. The only species observed by NMR and IR spectroscopy
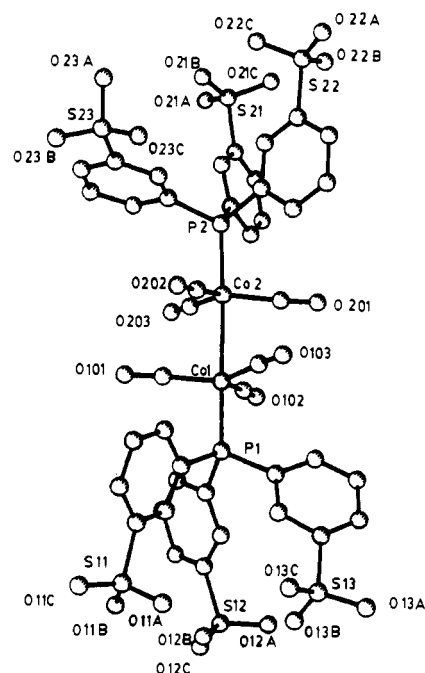
in the liquid phase is the monosubstituted hydride, **4**. Characteristic infrared and ^1H NMR spectra for $HCo(CO)_3[TPPTS-(H)]$, where $TPPTS(H) = P(m\text{-}C_6H_4SO_3H)_3$, are shown in Figure 2a. The carbonyl region of the infrared spectrum clearly shows the A_1 and E bands expected for C_{3v} symmetry. The $^{31}P-^1H$ coupling ($J_{PH} = 46.2$ Hz) observed by NMR spectroscopy is consistent with other cobalt hydrides.

The direct substitution of $HCo(CO)_4$ with triphenylphosphine occurs rapidly at –80 °C without any evidence for the formation of intermediates.[25] However, more basic phosphines, such as $P(nBu)_3$, initially yield $[HPR_3][Co(CO)_4]$, which slowly loses CO and forms $HCo(CO)_3PR_3$.[25] Attempts to directly substitute $HCo(CO)_4$ with TPPTS are complicated by the fact that $HCo-(CO)_4$ has limited water solubility and is dissociated at pH 7. Thus at neutral pH the substitution of $HCo(CO)_4$ with TPPTS in a two phase system could not be achieved. In the solvent mixture of THF and 5–10% H_2O (pH = 1), the direct substitution of $HCo(CO)_4$ with the acid form of TPPTS is successful. Under these conditions, the dissociation of the hydride is avoided; furthermore $HCo(CO)_3[TPPTS(H)]$ is soluble in this medium.

The two-phase synthesis of $HCo(CO)_2[TPPTS(H)]_2$, as described in the Experimental Section, also is accomplished at low pH. The acid form of TPPTS, $TPPTS(H)$, generated in the water phase at low pH, reacts with $HCo(CO)_4$ to yield the stable disubstituted cobalt hydride (Scheme I). Under these reaction conditions, we observe only the disubstituted hydride, which suggests that the substitution of the second CO is very fast. This is surprising because the disubstitution of $HCo(CO)_4$ with PPh_3 cannot be realized under similar conditions due to steric crowding.

Important spectroscopic proof for the existence of the hydrides, $HCo(CO)_3[TPPTS(H)]$ and $HCo(CO)_2[TPPTS(H)]_2$, is summarized in Figure 2. From the synthetic work presented here and the work of Herrmann et al.[1] on $HCo(CO)(TPPTS)_3$, the relative stability of water-soluble cobalt carbonyl hydrides is $HCo-(CO)_3[TPPTS(H)] < HCo(CO)_2[TPPTS(H)]_2 < HCo(CO)-(TPPTS)_3$. The preparation and characterization of the hydrides in water are significant, since the ability to do phosphine-modified cobalt carbonyl catalysis in water requires their presence. For both hydrides, a trigonal bipyramidal structure is likely. Sub-

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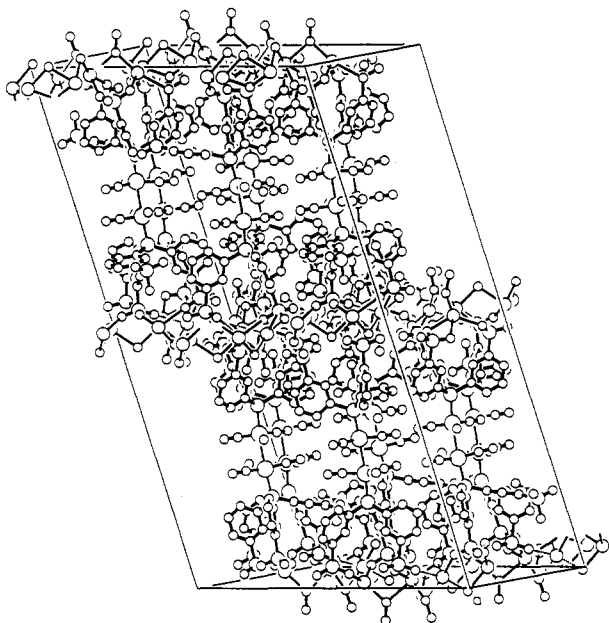
Figure 4. Cell packing diagram for **2**. The projection emphasizes the layered nature of the structure. The sulfonate groups show ionic interactions with sodium ions in the interlayer region. The sodium ions are further coordinated by water and methanol.

stitution of one CO occurs in the axial position trans to the H atom; the second substitution occurs in the equatorial plane. Two shoulders in the v_{CO} stretching pattern of **5** are apparent; these may be due to the presence of a bis equatorial disubstituted isomer.

Interestingly the aromatic carbon atoms of TPPTS(H) in **5** appear as pseudotriplets except for the carbon para to phosphorus. The pseudotriplets are proof of two phosphine ligands that are magnetically equivalent on the NMR time scale.

Qualitative Aspects of the Structure of 2. A view of the geometry about cobalt and the orientation of the phenyl rings is given in Figure 3; a packing diagram is shown in Figure 4. The packing diagram clearly shows the layered nature of the structure. Additional figures, including diagrams of the coordination geometry of the interlayer sodium ions, are available as supplementary material.

The sulfonated-phosphine-substituted cobalt dimer is composed of two trigonal bipyramidal Co atoms with the phosphine ligands in axial positions trans to a normal Co–Co bond (Figure 3). All bond distances and angles within the $Co_2(CO)_6L_2$ portion of the structure are normal. The trigonal planar array of CO groups on each Co atom are staggered with respect to each other. This arrangement is exactly that predicted on the basis of data for other compounds of the same class.[26] The layered structure, as shown in the packing diagram, consists of hydrophilic planes of sodium cations, solvent, and the sulfonate groups separated by hydrophobic planes of $Co_2(CO)_6L_2$. The overall appearance of the structure has some similarity to that observed for the smectite clays.[27] A similar layered arrangement of metal complex and sulfonate groups was observed in the crystal structure of $K_3\{Pd[PPh_2(m\text{-}C_6H_4SO_3)_3]\}$.[11]

The layered structure of **2** provides a model for supported-aqueous-phase (SAP) catalysts generated from the sodium salt of transition metal TPPTS complexes in the following sense. The sodium sulfonate groups in the structure are strongly associated with an aqueous layer. It is reasonable to suppose that a similar arrangement is present on the surface of SAP materials. That is, the sulfonate groups are likely to be strongly associated with adsorbed water while the metal portion of the complex is directed away from the surface.

Supplementary Material Available: A discussion of sodium ion geometries, Figures S1–S6, showing the coordination geometry of the six sodium cations in the lattice, and complete listings of atomic and thermal parameters, data collection parameters, and bond distances and angles (35 pages). Ordering information is given on any current masthead page.

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