

Synthesis and characterization of $\text{Na}_5[\text{Co}(\text{CO})_3(\text{P}((\text{CH}_2)_n\text{C}_6\text{H}_4\text{-p-SO}_3)_3)_2]$, $n = 1, 2, 3,$ and 6 . Novel zwitterionic cobalt(I) complexes and their use as precursors to water soluble hydroformylation catalysts

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Abstract

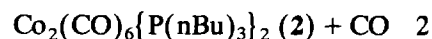
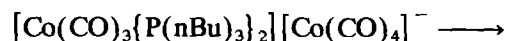
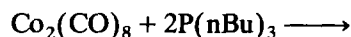
The electron donating water soluble phosphines, $\text{P}((\text{CH}_2)_n\text{C}_6\text{H}_4\text{-p-SO}_3\text{Na})_3, n = 1, 2, 3$ and 6 , react rapidly with $\text{Co}_2(\text{CO})_8$ under two phase reaction conditions to yield the disproportionation products, $[\text{Co}(\text{CO})_3(\text{P}((\text{CH}_2)_n\text{C}_6\text{H}_4\text{-p-SO}_3\text{Na})_3)_2][\text{Co}(\text{CO})_4]$. Selective precipitation yields the formally zwitterionic complex anions as the sodium salt, $[\text{Co}(\text{CO})_3(\text{P}((\text{CH}_2)_n\text{C}_6\text{H}_4\text{-p-SO}_3)_3)_2]^{5-}$. The anions can be used as precursors to water soluble cobalt hydroformylation catalysts under two phase and supported aqueous phase conditions. The tendency to form alcohol products is low with these complexes. The behavior of the catalysts is consistent with an active species that remains water soluble during the reaction and is not leached into the nonaqueous phase.

Key words: Cobalt; Carbonyl; Water-soluble phosphines; Hydroformylation; Water-soluble catalysts

1. Introduction

The substitution of CO in dicobalt octacarbonyl by phosphines and other nucleophiles is a well studied reaction [1–7]. With basic phosphines and phosphites the disproportionation product, $[\text{Co}(\text{CO})_3\text{L}_2][\text{Co}(\text{CO})_4]$, is observed as a reaction intermediate and in some cases can be isolated [8,9]. Metathesis with iodide or tetraphenylborate prevents reproporationation to $\text{Co}_2(\text{CO})_6\text{L}_2$ and allows the isolation of the $[\text{Co}(\text{CO})_3\text{L}_2]^+$ cation [10–12]. The reactions with $\text{P}(\text{nBu})_3$ are typical; these are shown in eqns. (1) and (2). The ionic intermediate, 1, is reported to be thermally unstable [5]. In general the reaction represented by (2) is fast for

monodentate phosphines. The cation, $[\text{Co}(\text{CO})_3\{\text{P}(\text{nBu})_3\}_2]^+$, can be isolated as the BPh_4^- salt [8–10].



When $\text{Co}_2(\text{CO})_8$ is substituted by the water soluble phosphine, TPPTS (TPPTS = trisulfonated triphenylphosphine trisodium salt) the ionic intermediate, $[\text{Co}(\text{CO})_3(\text{TPPTS})_2][\text{Co}(\text{CO})_4]$ is also observed [13]. Qualitatively it is more stable than its water insoluble triphenylphosphine analog; complete conversion of the ionic intermediate to the dimer, $\text{Co}_2(\text{CO})_6(\text{TPPTS})_2$, requires heating under partial vacuum [13].

Phosphine modified cobalt carbonyl hydroformylation catalysts require electron donating phosphines, such as $\text{P}(\text{nBu})_3$, to give good selectivity to linear alcohols [14]. Our interest in water soluble hydroformy-

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lation catalysts [15,16] led us to investigate the chemistry of the water soluble electron donating phosphines, P((CH₂)_nC₆H₄-*p*-SO₃Na)₃, *n* = 1, 2, 3, 6 (**3a–d** respectively) [17] with cobalt carbonyl.

Here we show that the basic water soluble phosphines, **3a–d**, react with Co₂(CO)₈ to yield [Co(CO)₃(P((CH₂)_nC₆H₄-*p*-SO₃Na)₃)₂][Co(CO)₄] (**4a–d**). Unlike the TPPTS analog (see above) the compounds represented by **4** do not undergo a reproporationation reaction. Furthermore, **4a–d** undergo an internal methathesis reaction to yield the formally zwitterionic complexes Na₅[Co(CO)₃(P((CH₂)_nC₆H₄-*p*-SO₃)₃)₂] (**5a–d**). In addition the complexes **5a–d** were investigated as precursors to water soluble hydroformylation catalysts.

2. Experimental section

All manipulations were carried out under a prepurified argon or carbon monoxide atmosphere by standard Schlenk techniques. The solvents, toluene, octene-1, and nonane, were distilled under argon before use. Dicobalt octacarbonyl was used as received from Strem Chemical Company; octene-1, nonane, and the sodium salt of dodecylbenzene sulfonic acid were obtained from Aldrich; and CO/H₂ (50/50) was received from Airco and used without further purification. The cobalt compounds, HCo(CO)₄ [18] and Na[Co(CO)₄] [19] and the phosphines **3a–d** [17] were synthesized by literature methods. Infrared spectra in water were recorded on a Nicolet 5DX spectrometer in transmission cells equipped with IRTRAN2 windows. The pathlength was 0.1 mm. The spectra were referenced to water to eliminate the water bending mode at 1640 cm⁻¹. Carbonyl bands in the region 2150 to 1800 cm⁻¹ were readily observed. NMR spectra were recorded on a Bruker WP 200 NMR spectrometer at observation frequencies of 200.133, 50.323, and 81.015 MHz for ¹H, ¹³C, ³¹P respectively. Protons and carbons are numbered consecutively from the phosphorus atom with the alpha carbon labeled (1)C.

2.1. Synthesis of Na₅[Co(CO)₃(P((CH₂)_nC₆H₄-*p*-SO₃)₃)₂], *n* = 1, (**5a**), *n* = 2, (**5b**), *n* = 3, (**5d**), *n* = 6, (**5d**)

A toluene solution of Co₂(CO)₈ (0.34 g, 1 mmol in 10 ml) was added to 10 ml of an aqueous solution containing 2 mmol of the appropriate phosphine, P((CH₂)_nC₆H₄-*p*-SO₃Na)₃. The two phase mixture was vigorously stirred under argon. With time the aqueous phase became dark brown. After 1 to 2 h the phases were separated and the aqueous layer was washed three times with 10 ml pentane. The brown water layer was concentrated to 2 ml and 20 ml THF was added.

The precipitate was collected and redissolved in 2 ml water. Repeated precipitation with THF was carried out until the precipitated solid was free of [Co(CO)₄]⁻ as determined by IR spectroscopy. The isolated yields, based on phosphine, were in the range of 80% to 90%. All compounds retain solvents, water and small quantities of THF, as detected by NMR spectroscopy; compound **5c** gave analytical results that suggest it is isolated as the pentahydrate.

5a; yellow powder. ¹H NMR δ (D₂O): 3.25 (s, 12H, (1)CH₂), 7.28 (s, br, 12H, (3)CH + (7)CH), 7.79 (s, br, 12H, (4)CH + (6)CH). ¹³C NMR δ (D₂O): 36.00 (t, J_{PC} = 13.1 Hz, (1)CH₂), 134.34 (s, (2)C), 126.21 (s, (3)CH + (7)CH), 130.98 (s, (4)CH + (6)CH), 142.65 (s, (5)C-SO₃Na), 190.74 (t, J_{PC} = 24.5 Hz, 3C CO). ³¹P NMR δ (D₂O): 66.74. IR ν_{CO}(D₂O): 2071.1vww, 2013.7vs, 2003.1vs cm⁻¹.

5b; yellow powder. ¹H NMR δ (D₂O): 2.62(s, br, 12H, (1)CH₂), 3.00 (s, br, 12H, (2)CH₂), 7.39 (s, br, 12H, (4)CH + (8)CH), 7.77 (s, br, 12H, (5)CH + (7)CH). ¹³C NMR δ (D₂O): 27.55 (s, br, (1)CH₂), 31.83 (s, br, (2)CH₂), 143.98 (s, (3)C), 128.68 (s, (4)CH + (8)CH), 131.13 (s, (5)CH + (7)CH), 145.40 (s, (6)C-SO₃Na), 196.81 (t, J_{PC} = 25.3 Hz, 3C, CO). ³¹P NMR δ (D₂O): 51.23. IR ν_{CO}(D₂O): 2070.0vww, 2009.3vs, 1996.1vs cm⁻¹.

5c; yellow powder. ¹H NMR δ (D₂O): 1.62 (s, br, 12H, (1)CH₂), 1.88 (s, br, 12H, (2)CH₂), 2.67 (s, br, 12H, (3)CH₂), 7.19, 7.23 (d[⊙], 12H, (5)CH + (9)CH), 7.69, 7.72 (d[⊙], 12H, (6)CH + (8)CH). ¹³C NMR δ (D₂O): 25.03 (s, (1)CH₂), 26.91 (t, J_{PC} = 15.6 Hz, (2)CH₂), 35.23 (t, J_{PC} = 7.5 Hz, (3)CH₂), 140.70 (s, (4)C), 125.81 (s, (5)CH + (9)CH), 129.07 (s, (6)CH + (8)CH), 144.70 (s, (7)C-SO₃Na), 193.69 (t, J_{PC} = 25.1 Hz, 3C, CO). ³¹P NMR δ (D₂O): 53.53. IR ν_{CO}(D₂O): 2067.6vww, 2003.1vs, 1994.9vs cm⁻¹. Elemental analysis: calc. for C₅₇H₆₀CoNa₅O₂₁P₂S₆ · 5H₂O: C 42.51; H 4.51; found: C 42.56; H 4.39%.

5d; yellow powder. ¹H NMR δ (D₂O): 1.05–1.60 (m, 60H, (1-5)CH₂), 7.13 (s, br, 12H, (8)CH + (12)CH), 7.71 (s, br, 12H, (9)CH + (10)CH). ¹³C NMR δ (D₂O): 26.10 (t, J_{PC} = 13.1 Hz, (1)CH₂), 28.15 (t, J_{PC} = 7.1 Hz, (2)CH₂), 32.21 (t, J_{PC} = 12.3 Hz, (3)CH₂), 31.30 (s, (4)CH₂), 33.41 (s, 6C, (s)CH₂), 37.83 (s, (6)CH₂), 143.12 (s, (7)C), 128.33 (s, (8)CH + (12)CH), 131.24 (s, (9)CH + (11)CH), 148.61 (s, (10)C-SO₃Na), 193.51 (t, J_{PC} = 25.5 Hz, CO). ³¹P NMR δ (D₂O): 53.26. IR ν_{CO}(D₂O): 2066.3vww, 1998.4vs, 1982.0vs cm⁻¹.

2.2. Catalytic reactions

High pressure catalytic reactions were carried out in stainless steel 30 ml Whitey sample cylinders fitted with appropriate pressure valves and gauges. An OMEGA CN 2000 temperature process controller was

used for the temperature control of the silicone oil bath. Magnetic stirring at a constant rate of 360 rpm was used in all catalytic runs. The reaction product analysis was done on a Varian 3300 gas chromatograph equipped with a HPI column (25 m × 0.32 mm × 0.52 μm) and FID detector. The carrier gas was helium and the temperature program was from 50°C (3 min) to 200°C (5 min), at a heating rate of 10°C/min. The products were further identified by GC-MS spectroscopy on a VG 7070E-HF instrument.

Stock solutions of the reactants were prepared and stored under argon as follows: The phosphines, P((CH₂)_nC₆H₄-*p*-SO₃Na)₃, *n* = 1, 2, 3, 6 were prepared as 0.20 M solutions in water; the cobalt zwitterions, **5a–c**, 0.10 M in water. The concentration of the catalyst on the controlled pore glass for the supported aqueous phase, SAP [15], systems was 0.05 mmol [Co]/g glass. The supported cobalt catalysts were prepared in the manner described for cobalt TPPTS catalysts [16]. In a typical reaction the organic phase contained 0.6 ml (3.82 mmol) of octene-1, 0.34 ml of nonane as an internal standard for the GC analysis and sufficient toluene to bring the total volume to 2 ml. The aqueous phase, 2 ml, contains **5a–c** and the appropriate excess phosphine; octene-1: Co = 250 (a bulk

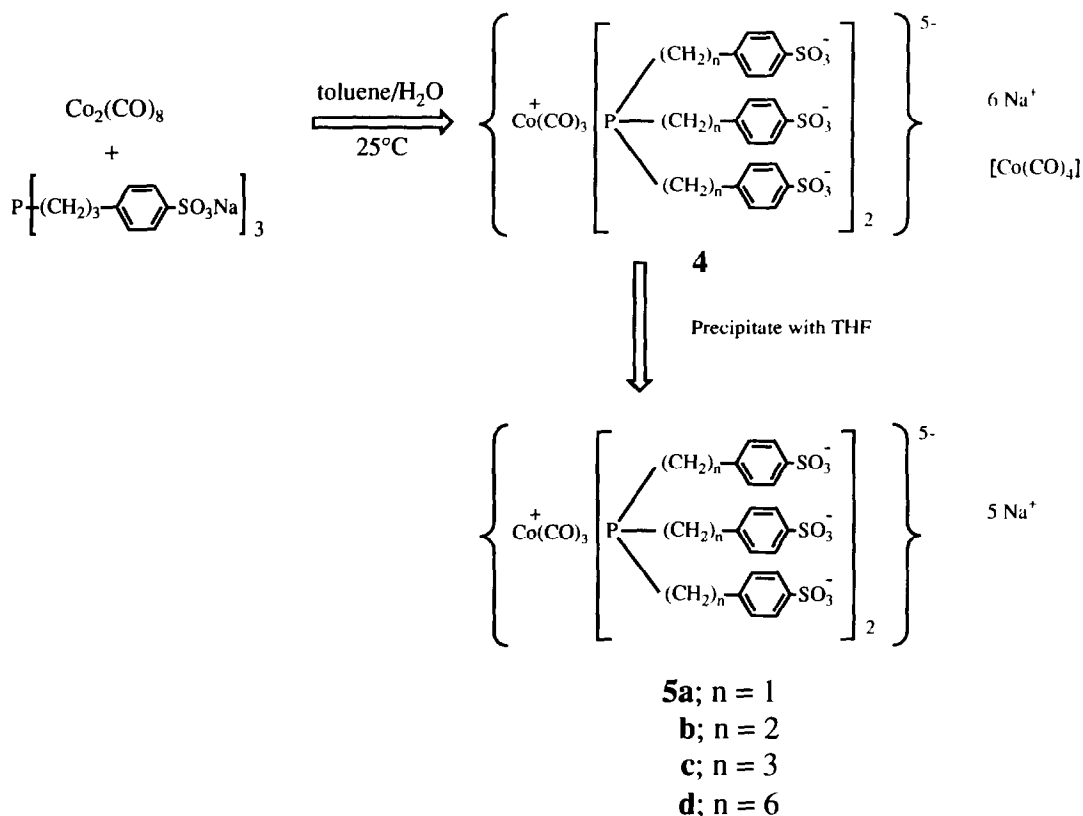
aqueous phase was not added to the SAP catalysts). The steel cylinders were pressurized to 15 atm at room temperature and then immersed in an oil bath that had been preheated to 190°C. All catalytic reactions were run for 14 h; the pressure drop during the catalytic reactions was less than 10 percent.

3. Results and discussion

3.1. Complex synthesis

The reaction of dicobalt octacarbonyl with the trisulfonated tris(*ω*-phenylalkyl) phosphines, P((CH₂)_n-C₆H₄-*p*-SO₃Na)₃ where *n* = 1, 2, 3 or 6, occurs under two phase reaction conditions according to Scheme 1. Cobalt is efficiently extracted from toluene solutions of Co₂(CO)₈ by aqueous solutions of P((CH₂)_nC₆H₄-*p*-SO₃Na)₃; with vigorous stirring the transfer is complete within 30 min. Infrared spectroscopy is consistent with the formation of only [Co(CO)₃(P((CH₂)_nC₆H₄-*p*-SO₃Na)₃)₂][Co(CO)₄] (**4**) in the aqueous phase. Neither heating under vacuum nor refluxing in water/THF solution converts **4** to the corresponding dimer, Co₂(CO)₆(PR₃)₂.

The water soluble phosphines are used as the sodium salt in the synthesis above and all of the water soluble



Scheme 1.

products of the reaction are expected to be strong electrolytes. Thus in aqueous solution the following ionic species are present; $[\text{Co}^+(\text{CO})_3(\text{P}((\text{CH}_2)_n\text{C}_6\text{H}_4\text{-}p\text{-SO}_3^-)_3)_2]^{5-}$, $[\text{Co}(\text{CO})_4]^-$, and 6 Na^+ . The first of these has a net five minus charge since it is a complex of cobalt(I). Therefore the solutions contain $\text{Na}[\text{Co}(\text{CO})_4]$ which has appreciable solubility in THF. Exhaustive dissolution and precipitation from aqueous THF yields $\text{Na}_5[\text{Co}(\text{CO})_3(\text{P}((\text{CH}_2)_n\text{C}_6\text{H}_4\text{-}p\text{-SO}_3)_3)_2]$ (5) as a solid precipitate while $\text{Na}[\text{Co}(\text{CO})_4]$ remains in solution.

NMR spectroscopy (^{31}P and ^{13}C) as well as infrared spectroscopy are consistent with formulation of **5a-d** as $\text{Na}_5[\text{Co}(\text{CO})_3(\text{P}((\text{CH}_2)_n\text{C}_6\text{H}_4\text{-}p\text{-SO}_3)_3)_2]$. Spectra are presented in Fig. 1 for $n = 3$, **5c**. Three bands are observed in the carbonyl region of the IR spectrum. This is consistent with a pyramidal tricarbonyl group with mirror plane symmetry as would be expected for one phosphine in the equatorial plane and one in an axial position. The five coordinate complex is likely to be fluxional on the NMR timescale; this accounts for the observation of a single ^{31}P NMR signal for the

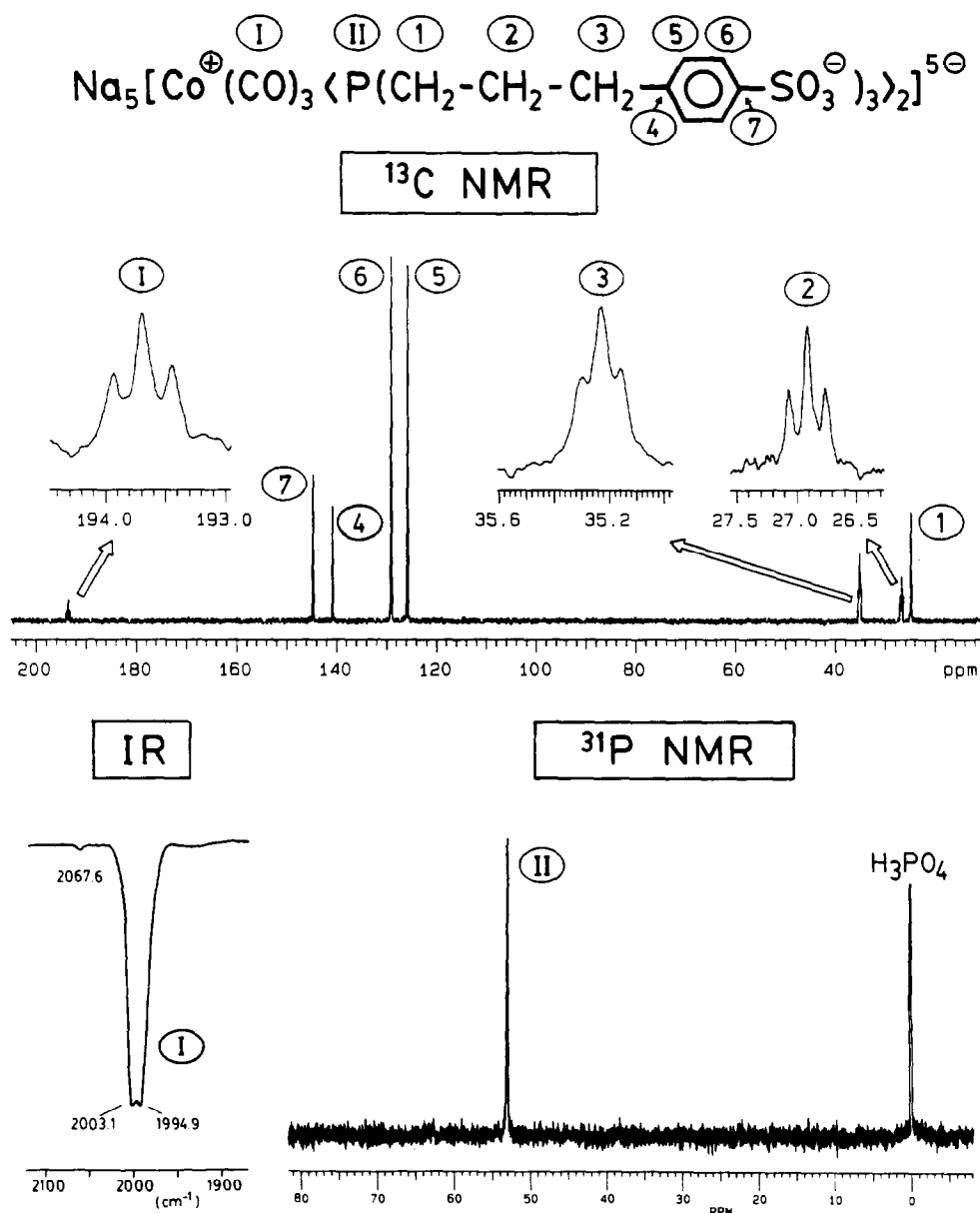


Fig. 1. Selected portions of the ^1H , ^{13}C , and ^{31}P NMR spectra, and the infrared spectrum in the carbonyl region, with the appropriate assignments for compound **5c**.

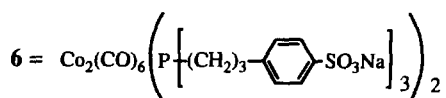
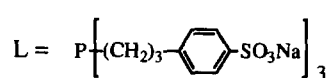
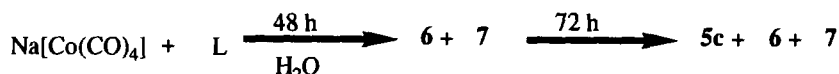
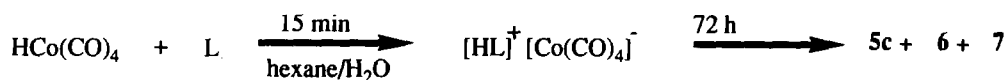
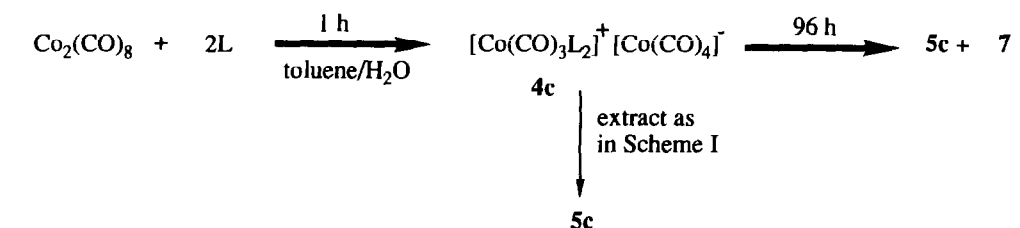
phosphines and the triplet in the carbonyl region of the ¹³C NMR spectrum. Low temperature NMR studies are not possible for these compounds since water must be used as the solvent or cosolvent. The ¹³C NMR signals of the methylene groups are assigned based on chemical shift; the carbon bonded to the phenyl group is assigned to the most downfield aliphatic carbon signal. Some of the carbon signals clearly appear as virtual triplets consistent with coupling to magnetically equivalent phosphorus atoms. Phosphorus-carbon coupling constants depend on the relationship to the lone pair at phosphorus, coordination to cobalt in the compounds prepared here apparently diminishes the absolute magnitude of the P-C coupling [20].

The series of compounds represented by **5** is significant in that the ease of preparation and isolation of the complexes stems from the unique properties of the sulfonated water soluble phosphines P[(CH₂)_nC₆H₄-*p*-SO₃Na]₃. Specifically the basic phosphines induce disproportionation and water as a solvent stabilizes the disproportionated products, **4**. The presence of aryl-sulfonate groups allows a simple metathesis reaction to take place to yield **5**.

For the phosphine $n = 3$, **3c**, further reaction chemistry with HCo(CO)₄ and Na[Co(CO)₄] was explored.

The results from these experiments are summarized in Scheme 2. The two-phase reaction of **3c** with HCo(CO)₄ results in the immediate formation of [HP[(CH₂)₃-C₆H₄-*p*-SO₃Na]₃]Co(CO)₄ in the aqueous phase. This intermediate is easily recognized by its ³¹P NMR spectrum, which shows a signal at 12.71 ppm for the phosphonium ion, and its infrared spectrum which has only one band, $\nu_{\text{CO}} = 1911.7 \text{ s cm}^{-1}$, consistent with tetracarbonyl cobaltate. Slowly, over three days, a mixture of **5c**, Co₂(CO)₆[P[(CH₂)₃C₆H₄-*p*-SO₃Na]₃]₂ (**6c**), and a species, **7**, which appears to contain a new phosphonium ion, is obtained. The dimer, **6c**, could not be isolated in pure form from this mixture and was identified only by its infrared and NMR spectra; $\nu_{\text{CO}} = 1941 \text{ cm}^{-1}$, and ³¹P NMR, $\delta = 60.6 \text{ ppm}$.

When **3c** reacts with Na[Co(CO)₄] in the aqueous phase again a mixture of **5c**, **6c**, and **7** is obtained. Also shown in Scheme 2 is the fact that prolonged reaction times of **3c** with Co₂(CO)₈ yields the compound designated **7**. Compound **7** is characterized by a sharp signal in its ³¹P NMR spectrum at 23.01 ppm. Small quantities of **7** could be separated from **5c** by repetitive precipitation; the infrared spectrum of **7** shows no bands in the carbonyl stretching region. All attempts to purify and isolate the dimer, **6c**, from reactions that



Scheme 2.

TABLE 1. Hydroformylation of Hexene-1 with Na₅[Co⁺(CO)₃L₂]⁵⁻

Conditions	Compound	L	P/Co	Ald. conv. (%)	n/b	Alc. conv. (%)
T	5a	P(CH ₂ C ₆ H ₄ - <i>p</i> -SO ₃ Na) ₃	2	34.3	1.2	1.2
W	5b	P[(CH ₂) ₂ C ₆ H ₄ - <i>p</i> -SO ₃ Na] ₃	2	35.2	1.1	3.0
O	5c	P[(CH ₂) ₃ C ₆ H ₄ - <i>p</i> -SO ₃ Na] ₃	2	38.0	1.2	2.6
P						
H	5a	P(CH ₂ C ₆ H ₄ - <i>p</i> -SO ₃ Na) ₃	5	24.6	1.9	0.4
A	5b	P[(CH ₂) ₂ C ₆ H ₄ - <i>p</i> -SO ₃ Na] ₃	5	28.7	2.3	0.4
S	5c	P[(CH ₂) ₃ C ₆ H ₄ - <i>p</i> -SO ₃ Na] ₃	5	34.5	3.6	0
E						
S	5c	P[(CH ₂) ₃ C ₆ H ₄ - <i>p</i> -SO ₃ Na] ₃	2	55.1	1.5	0
A	5a	P(CH ₂ C ₆ H ₄ - <i>p</i> -SO ₃ Na) ₃	5	37.5	2	0
P	5b	P[(CH ₂) ₂ C ₆ H ₄ - <i>p</i> -SO ₃ Na] ₃	5	42.1	2.4	0
	5c	P[(CH ₂) ₃ C ₆ H ₄ - <i>p</i> -SO ₃ Na] ₃	5	44.3%	3.6	0

gave this compound as one of the products were unsuccessful.

3.2. Olefin hydroformylation

The results obtained for hexene-1 and octene-1 hydroformylation with **5a–d** are summarized in Tables 1 and 2. In each comparison of a two-phase catalytic reaction and its supported aqueous phase counterpart with the same complex as the catalyst, the total cobalt and reaction stirring rates were kept constant. Thus at a constant reaction time the conversion gives a rough measure of the reaction rate. In general the supported aqueous phase catalysts showed higher activity than the two phase catalysts. This effect was more pronounced with octene-1 compared to hexene-1 as the substrate.

For each phosphine studied the catalytic activity decreases and the n/b ratio increases as the L/Co ratio is increased. This is the expected behavior for

phosphine modified cobalt catalysts. Several features of the water soluble catalysts derived from the electron donating phosphines however are unusual.

The n/b ratio never approaches that expected for a phosphine modified cobalt catalyst in the nonaqueous phase [14]. Also the reaction both in the supported aqueous phase and under two phase reaction conditions gives almost exclusively aldehyde and very little or no alcohol product. Alcohols are the expected products for phosphine modified cobalt hydroformylation catalysts in nonaqueous solvents. At first inspection these observations suggest that unmodified cobalt carbonyl, formed *in situ*, may be responsible for the catalysis. However reaction activity and selectivity are dependent on the L/Co ratio which is consistent with retention of cobalt phosphine complexes during catalysis. More importantly, unmodified cobalt carbonyl is not water soluble and would be expected to leach

TABLE 2. Hydroformylation of Octene-1 with Na₅[Co⁺(CO)₃L₂]⁵⁻

Conditions	Compound	L	P/Co	Ald. conv. (%)	n/b	Alc. conv. (%)
T	5a	P(CH ₂ C ₆ H ₄ - <i>p</i> -SO ₃ Na) ₃	2	4.1	1.9	0
W	5b	P[(CH ₂) ₂ C ₆ H ₄ - <i>p</i> -SO ₃ Na] ₃	2	4.8	1.9	0
O	5c	P[(CH ₂) ₃ C ₆ H ₄ - <i>p</i> -SO ₃ Na] ₃	2	6.2	2.0	0
	5d	P[(CH ₂) ₆ C ₆ H ₄ - <i>p</i> -SO ₃ Na] ₃	2	7.3	2.1	0
P						
H						
A	5c	P[(CH ₂) ₃ C ₆ H ₄ - <i>p</i> -SO ₃ Na] ₃	5	5.0	2.4	0
S	5d	P[(CH ₂) ₆ C ₆ H ₄ - <i>p</i> -SO ₃ Na] ₃	5	6.1	2.5	0
E						
	5c	P[(CH ₂) ₃ C ₆ H ₄ - <i>p</i> -SO ₃ Na] ₃	2	57.1	0.6	2.5
S	5d	P[(CH ₂) ₆ C ₆ H ₄ - <i>p</i> -SO ₃ Na] ₃	2	58.5	0.7	2.8
A						
P	5c	P[(CH ₂) ₃ C ₆ H ₄ - <i>p</i> -SO ₃ Na] ₃	5	22.4	2.4	0
	5d	P[(CH ₂) ₆ C ₆ H ₄ - <i>p</i> -SO ₃ Na] ₃	5	24.1	1.1	0
	5d	P[(CH ₂) ₆ C ₆ H ₄ - <i>p</i> -SO ₃ Na] ₃	7	7.5	2.3	0
	5d	P[(CH ₂) ₆ C ₆ H ₄ - <i>p</i> -SO ₃ Na] ₃	10	2.2	2.6	0

significantly into the nonaqueous phase. The two-phase and SAP reactions with hexene-1 as the substrate were examined for cobalt leaching into the nonaqueous phase. This was accomplished by analysis of the nonaqueous phase by atomic absorption spectroscopy and by recycling the nonaqueous phase with heptene-1 added as the substrate. With the donor phosphine complexes, **5**, both tests were negative; *i.e.* no cobalt could be detected by atomic absorption spectroscopy and no heptene-1 conversion was observed in the recycled solutions. It is estimated that leaching of one percent of the total cobalt could be detected by the methods used. The level of activity of the SAP and the two phase catalysts is not consistent with a small amount of leached cobalt. These experiments are most consistent with a water soluble catalytically active species.

Water has been observed to have an effect on nonaqueous phosphine modified cobalt catalysts [21,22]. Addition of water to P(nBu)₃ modified cobalt carbonyl catalysts increases the rate of alcohol formation at low conversion. This effect is not seen in the water soluble catalysts investigated here.

The immediate catalyst precursor in each case was the zwitterionic series of compounds, **5a–d**. These are not the typical precursors for phosphine modified cobalt hydroformylation catalysts and the unusual selectivities may be related to the nature of the cobalt complexes responsible for the catalysis.

Previously it has been shown that the cobalt dimer, Co₂(CO)₆(TPPTS)₂, can be used as a precursor to water soluble hydroformylation catalysts both in the supported aqueous phase [16] and under two phase conditions [23]. The present catalysts differ in that the synthetic precursor to the catalysts is not the dimer but rather the ionic compounds represented by **5**. Although evidence for the dimer, **6c**, was obtained in some syntheses, it could not be isolated. The nature of the water soluble cobalt complexes of the electron donating water soluble phosphines that may be formed under catalytic conditions is not known, although it is

likely that cobalt hydrides are formed in aqueous solution under hydroformylation conditions.

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