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# Preparation and Properties of Anionic Transition Metal Complexes Containing Triheterocarbenium Ions

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## Summary

Thermally stable anionic tetracarbonylcobalt complexes containing triheterocarbenium ions, $[Co(CO)_4]^-[cation]^+$, have been synthesized by the ion exchange reaction of $[Co(CO)_4]^-PPN^+$ with the corresponding carbenium ions. Similar molybdenum complexes containing cyclopentadienyl and carbonyl ligands were also prepared. The complexes were characterized by elemental analyses and by i.r. and n.m.r. spectroscopies. The ionic structures of the complexes are confirmed on the basis of their large electric conductivities.

## Introduction

Most transition metal-carbon bonds are generally considered to be polarized in the sense $M^{\delta+}$ and $C^{\delta-}$, and studies of transition metal-alkyls have been investigated in the context of transition metal catalyzed reactions(1, 2). However, attempts to prepare and to utilize organotransition metal compounds having a metal-carbon bond polarized in the reverse sense ($M^{\delta-}$–$C^{\delta+}$) have been less explored.

As the first step in attempting to prepare organotransition metal compounds having such a metal-to-carbon bond, we have investigated reactions between anionic transition metal complexes, *e.g.*, $[Co(CO)_4]^-$, $[MoCp(CO)_3]^-$, and carbenium ions stabilized by three electron donating heteroatoms such as S and N, *e.g.*, $[\overline{SCH_2CH_2SC}NMe_2]^+$ (4, 5).

We now report the isolation and characterization of thermally stable cobalt and molybdenum anionic complexes having carbenium ions as the counter cation.

## Results and Discussion

2-Dimethylamino-1,3-dithiolanylium tetracarbonyl cobaltate $[\overline{SCH_2CH_2SC}NMe_2]^+[Co(CO)_4]^-$ *(1)* was prepared by an ion exchange reaction between bis(triphenylphosphorus-μ-nitrido tetracarbonylcobaltate, $[(Ph_3P)_2N]^+[Co(CO)_4]^-$ ($PPN^+[Co(CO)_4]^-$)(6) and 2-dimethylamino-1,3-dithiolanilium tetraphenylborate in acetone at room temperature.

$$[\overline{SCH_2CH_2SC}NMe_2]^+[BPh_4]^- \; (7) \; + \; PPN^+[Co(CO)_4]^-$$
$$\downarrow$$
$$PPN^+[BPh_4]^- + [\overline{SCH_2CH_2SC}NMe_2]^+(Co(CO)_4]^- \qquad (1)$$

Similar exchange reactions of the $[Co(CO)_4]^-$ anion with other triheterocarbenium ions also proceeded smoothly to yield the corresponding new ionic complexes. Use of $[MoCp(CO)_3]^-$ instead of $[Co(CO)_4]^-$ gave analogous complexes which were isolated as crystals and have considerably higher stabilities in air than do other salts of $[Co(CO)_4]^-$ and $[MoCp(CO)_3]^-$ with group I metal cations such as Na and K(3). Analytical, i.r. and $^1H$ n.m.r. data, together with some physical properties of the isolated anionic complexes having the carbenium counter ions are summarized in Table. The i.r. spectrum of *(1)* showed ν(C–N) at 1590 $cm^{-1}$ and strong ν(C≡O) bands at 2000, 1900, and 1870 $cm^{-1}$. Although several resonance forms (*e.g.*, $\overline{SCH_2CH_2SC}{=}N^+Me_2$ or $\overline{SCH_2CH_2SC}{}^+NMe_2$) can be written for the carbenium ion in *(1)*, the absence of a significant shift in the observed ν(C–N) from the wave numbers of ν(C–N) in the known cation *(7)* indicates that the carbenium ion in *(1)* is not in a greatly different electronic state from that in *(7)*. The $^1H$ n.m.r. spectrum of *(1)* in $CD_2Cl_2$ shows two singlets at 4.14(4H, $CH_2$) and 3.70(6H, Me), which are shifted downfield by 0.66–0.50 ppm from the signals found in $[\overline{SCH_2CH_2SC}NMe_2]^+[BPh_4]^-$ *(7)*. A similar downfield shift is also observed in *(3)*. These proton shifts may be due either to the enhanced delocalization of the positive charge on N and/or S, which occurs on the formation of the $[Co(CO)_4]^-$ and $[MoCp(CO)_3]^-$ salts, or to magnetic anisotropies of the highly electronegative transition metal anions. The appearance of these protons at significantly lower field, compared to the usual positions for methyl and methylene protons, has been interpreted in terms of delocalization of the positive charge on the hetero atoms(4). High electric conductivities of these complexes, shown in the Table, support their ionic structure and exclude the possibility of covalent bond formation between the carbon and the transition metal.

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**Table 1.** Analytical and spectroscopic data for transition metal anionic complexes with carbenium counter ions.

| Complex | Found (Calcd.)% C | H | N | Yield (%) | M.p. (°) | Color | E.E.[b] | I.r. (cm$^{-1}$) ν(C–N) | ν(C≡O) | $^1$H n.m.r. (ppm) | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| *(1)* $[\overline{SCH_2CH_2SC}NMe_2]^+[Co(CO)_4]^-$ | 34.2<br>(33.9) | 3.1<br>(3.1) | 4.4<br>(3.5) | 50 | 101–102[a] | yellow | 150 | 1590s | 2000w, 1900sh,<br>1870vs | $-C_2H_4-$<br>$NMe_2$ | 4.14s (4H)<br>3.70s (6H) |
| *(2)* $[o\text{-}\overline{SC_6H_4N(Me)C}H]^+[Co(CO)_4]^-$ | 44.4<br>(44.9) | 2.4<br>(2.5) | 4.2<br>(4.4) | 24 | 62–63[a] | orange | 190 | – | 1880vs | NMe<br>CH<br>$C_6H_4$ | 4.51s (3H)<br>10.08s (1H)<br>7.8–8.7m (4H) |
| *(3)* $[\overline{SCH_2CH_2SC}NMe_2]^+[MoCp(CO)_3]^-$ | 39.3<br>(39.7) | 3.9<br>(3.8) | 3.5<br>(3.6) | 58 | 115–119[a] | yellow | 130 | 1580s | 1890vs, 1760vs | $-C_2H_4-$<br>$NMe_2$<br>Cp | 3.96s (4H)<br>3.56s (6H)<br>4.96s (5H) |
| *(4)* $[o\text{-}\overline{SC_6H_4N(Me)C}H]^+[MoCp(CO)_3]^-$ | 48.5<br>(48.6) | 3.4<br>(3.3) | 3.6<br>(3.5) | 34 | 120–122[a] | red | | – | 1890vs, 1760vs | NMe<br>CH<br>$C_6H_4$<br>Cp | 4.70s (3H)[d]<br>10.58s (1H)<br>7.8–8.7m (4H)<br>4.98s (5H) |
| *(5)* $[(MeS)_2CNMe_2]^+[MoCp(CO)_3]^-$ | 40.0<br>(39.5) | 4.3<br>(4.3) | 3.5<br>(3.5) | 10 | 50–52[a] | red | | – | 1890vs, 1750vs | SMe<br>$NMe_2$<br>Cp | 2.98s (6H)<br>3.88s (6H)<br>5.16s (5H) |
| *(6)* $PPN^+[MoCp(CO)_3]^-$ | 67.0<br>(67.3) | 4.5<br>(4.5) | 1.7<br>(1.8) | 56 | 221–222 | yellow | 130 | – | 1890vs, 1760vs | Ph<br>Cp | 7.5–8.6m (30H)<br>4.90s (5H) |
| *(7)* $[\overline{SCH_2CH_2SC}NMe_2]^+[BPh_4]^-$ | | | | | | white | 90 | 1590s | – | $-C_2H_4-$<br>$NMe_2$<br>Ph | 3.48s (4H)<br>3.20s (3H)<br>7.0–7.5m (20H) |
| *(8)* $[o\text{-}\overline{SC_6H_4N(Me)C}H]^+[BPh_4]^-$ | | | | | | white | | – | – | NMe<br>CH<br>Ph<br>$C_6H_4$ | 4.55s (3H)[g]<br>10.17s (1H)<br><br>7.8–8.4m (24H) |

[a] Dec.; [b] Equivalent Electric Conductivity; [c] ohm$^{-1}$cm$^2$mol$^{-1}$ in $Me_2CO$ at 20°, $1.35 \times 10^{-5}$ mol · dm$^{-3}$; [d] KBr disc; [e] in $CD_2Cl_2$; [f] in $(CD_3)_2CO$; [g] in $CF_3CO_2D$.

The anionic complexes *(1–5)* so far exhibit low chemical reactivity toward various organic compounds, such as olefins, acetylenes, carbon monoxide, carbon dioxide, and epoxides; only the starting materials were recovered at ambient conditions from the reaction mixtures. This is probably due to the strong bond between the metal and the carbonyl ligands. Coordinatively unsaturated species which would be produced by dissociation of part of the ligands might be reactive. In contrast to the poor reactivities of *(1)* towards unsaturated molecules, metathesis of *(1)* with iodomethane took place smoothly to give $[\overline{SCH_2CH_2SC}NMe_2]^+I$, and, in the presence of both $PPh_3$ and CO, the methylcobalt intermediate formed simultaneously was trapped as a known acetyl cobalt complex $MeCOCo(CO)_3(PPh_3)_3$(7).

$$[\overline{SCH_2CH_2SC}NMe_2]^+[Co(CO)_4]^- + MeI$$
$$\downarrow$$
$$MeCo(CO)_4 + [\overline{SCH_2CH_2SC}NMe_2]^+I^-$$
$$\downarrow + PPh_3,\ CO$$
$$MeCOCo(CO)_3(PPh_3)$$

Complex *(3)* also reacted with MeI to give known nonionic $MeMoCp(CO)_3$(3).

## Experimental

All procedures were performed under nitrogen or argon. Solvents were purified by a usual manner and stored under nitrogen before use. I.r. spectra were recorded on a Hitachi 295 spectrometer and $^1$H n.m.r. spectra were measured on a JEOL PS-100 and PMX-60 spectrometers. Microanalyses were carried out by Mr. T. Saito of our research laboratory using a Yanagimoto CHN Autocorder Type MT-2. Equivalent electric conductivities were measured by using TOA conductivity meter model CM-5B. Triheterosubstituted carbenium tetraphenylborates(4), $PPN^+Cl$(6), $Na^+[Co(CO)_4]^-$(6) and $Na^+[MoCp(CO)_3]^-$(6) were synthesized by literature methods. I.r. and $^1$H n.m.r. spectroscopic data, yields, m.p's. and elemental analyse are listed in Table 1.

### *$PPN^+[MoCP(CO)_3]^-$ (6)*

$PPN^+Cl^-$ (7.0 mmol) in $CH_2Cl_2$ (20 cm$^3$) was added to a THF solution (30 cm$^3$) of $Na^+[MoCp(CO)_3]^-$ which was prepared from $Mo(CO)_6$ (10 mmol) and NaCp (10 mmol). After filtration of the resulting solution, $Et_2O$ (20 cm$^3$) was added to give a yellow solution. On cooling this solution at –20°, light yellow crystals were obtained.

### *$[\overline{SCH_2CH_2SC}NMe_2]^+[Co(CO)_4]^-$ (1)*

$PPN^+[Co(CO)_4]^-$ (2.0 mmol) in $Me_2CO$ (10 cm$^3$) was added to $[\overline{SCH_2CH_2SC}NMe_2]^+[BPh_4]^-$ (2.0 mmol) in $Me_2CO$ solution (100 cm$^3$) at room temperature. The volume of the solution was reduced to 20 cm$^3$ by evaporation and then an excess of hexane was added to give a red oil. After filtration of the resulted heterogeneous solution, solvent was removed *in vacuo* to give a red solid, which was recrystallized from $CH_2Cl_2 : Et_2O$.

Complex *(2)* was prepared analogously. Complex *(5)* was prepared in a similar manner at lower temperature (below 0 °).

*$[o\text{-}\overline{SC_6H_4N(Me)C}H]^+[MoCp(CO)_3]^-$ (4)*

To an $Me_2CO$ solution (30 $cm^3$) of $PPN^+[MoCp(CO)_3]^-$ (0.369 mmol) at –78° was added $[o\text{-}\overline{SC_6H_4N(Me)C}H]^+[BPh_4]^-$ (0.369 mmol). Raising the temperature to 0° resulted in a white precipitate ($PPN^+[BPh_4]^-$). After concentration to 3 $cm^3$, the solution was filtered and hexane (3 $cm^3$) was added to the filtrate. Cooling the solution to –40° gave red crystals, which was recrystallized from $Me_2CO$ : hexane as red needles. Complex *(3)* was prepared analogously.

*Reaction of (1) with MeI in the presence of CO*

MeI (1 $cm^3$) was added by trap-to-trap distillation to a mixture of complex *(1)* (0.0674 mmol) and $PPh_3$ (0.1348 mmol) in THF (5 $cm^3$). Then an excess of CO was introduced into the reaction vessel (1 atm). After filtration of the resulting mixture, solvent was removed *in vacuo* to yield a light green solid, $MeCOCo(CO)_3(PPh_3)^{(7)}$. I.r. $\nu(C{=}O)$ 1680 $cm^{-1}$.

*Reaction of (3) with MeI*

Treatment of *(3)* with MeI (1 $cm^3$) immediately gave a white precipitate. The excess of MeI was removed by evaporation *in vacuo*. Sublimation of the residual solid gave yellow crystals whose i.r. spectrum was identical with that of an authentic sample of $MeMoCp(CO)_3^{(3)}$.

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# Ethers as Ligands. Part VI. Transition Metal(II) Complexes with 18-Crown-6

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## Summary

Seven new coordination compounds are reported with the cyclic polyether 18-crown-6 as the ligand, *viz.* $[Mg(18\text{-crown-}6)(H_2O)_2](SbCl_6)_2$, $[M(18\text{-crown-}6)(MeNO_6)_2](SbCl_6)_2$ with M is $Ca^{2+}$ and $Sr^{2+}$, $[M(18\text{-crown-}6)(MeNO_2)](SbCl_6)_2$ with M is $Mn^{2+}$ and $Co^{2+}$, and $[M(18\text{-crown-}6)](SbCl_6)_2$ with M is $Ni^{2+}$ and $Zn^{2+}$.

## Introduction

During the last decade the properties of the cyclic polyether 18-crown-6, 1,4,7,10,13,16-hexaoxacyclooctadecane, have been investigated intensively. This crown ether already finds many applications in a wide variety of chemical reactions(1–3). The ligand properties of 18-crown-6 have also been studied and many reports have appeared dealing with 18-crown-6 complexes of mainly alkaline and alkaline earth metal ions(4–11). Several comples with first row transition metal ions have been reported also(4–6), but these compounds did not include solvates(12). It seemed therefore worthwhile to attempt to prepare transition metal solvates with 18-crown-6.

## Experimental

The ligand, 18-crown-6, was prepared by the method described by Gokel and Cram(13). $MeNO_2$ was used after storage over anhydrous $CaSO_4$. The complexes were prepared by adding solutions of 18-crown-6 (0.02 mole) in $CH_2Cl_2$ to solutions of $[M(MeNO_2)_6](SbCl_6)_2$ (0.01 mole) in $MeNO_2^{(14)}$. The resulting clear solutions were stored at – 6°. After some time crystals separated which were collected on a glass filter, washed with sodium-dried n-pentane and dried *in vacuo* at slightly elevated temperatures (not exceeding 50°). The compounds decompose rapidly in the presence of $H_2O$, therefore all manipulations were done in a $P_2O_5$-dried atmosphere. The

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