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REACTIONS OF ALKALI METAL DERIVATIVES OF METAL CARBONYLS X. THE NATURE OF THE PRODUCT FROM THE REACTION BETWEEN SODIUM TETRACARBONYLCOBALTATE(−1) AND TRIMETHYLCYCLOPROPENYL TETRAFLUOROBORATE*

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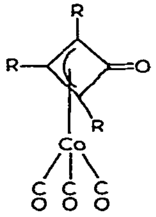
SUMMARY

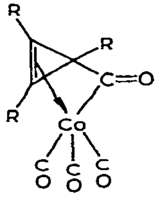
Trimethylcyclopropenyl tetrafluoroborate reacts with $NaCo(CO)_4$ in tetrahydrofuran solution to form yellow crystalline $(CH_3)_3C_3COCo(CO)_3$. The NMR chemical shifts of the methyl protons support formulation of this complex as a keto-π-cyclobutenyl derivative rather than a cyclopropenylcarbonyl derivative.

INTRODUCTION

In 1962 Coffey[2] reported the reaction between triphenylcyclopropenyl bromide and sodium tetracarbonylcobaltate to give a stable yellow solid of the composition $(C_6H_5)_3C_3COCo(CO)_3$. Two alternative structures (I) and (II) ($R = C_6H_5$) were suggested for this complex. The decision between these two alternative structures was equivocal:



(I)



(II)

however, the fact that degradation of an analogous iron complex $(C_6H_5)_3C_3COFe(CO)_2NO$ with 1,3-diphenylallyl chloride gave triphenylcyclopropenyl chloride was interpreted to favor structure (II) for the cobalt complex. In an attempt to clarify the nature of Coffey's complexes we have prepared the permethyl analogue $(CH_3)_3C_3COCo(CO)_3$ from trimethylcyclopropenyl tetrafluoroborate and $NaCo(CO)_4$. This

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note describes the spectroscopic properties of this permethylated cobalt complex. These data provide strong evidence that this complex as well as Coffey's original complexes are keto-π-cyclobutenyl derivatives (I) rather than cyclopropenylcarbonyl derivatives (II).

EXPERIMENTAL

A nitrogen atmosphere was routinely provided for the following operations: (a) carrying out reactions; (b) admitting to evacuated vessels; and (c) handling filtered solutions of organometallic derivatives. Trimethylcyclopropenyl tetrafluoroborate was prepared from 3-methyl-2,4-pentanedione via 3,4,5-trimethylpyrazole using the published procedure[3,4].

Reaction of sodium tetracarbonylcobaltate(−1) with trimethylcyclopropenyl tetrafluoroborate

A mixture of 1.0 g (2.93 mmoles) of octacarbonyldicobalt (Strem Chemical Co., Andover, Massachusetts), 0.3 g (13 mg-atoms) of sodium as a 5% amalgam, and 125 ml of redistilled (over $LiAlH_4$) tetrahydrofuran was stirred at room temperature for 90 min to form a solution of $NaCo(CO)_4$. After removal of excess amalgam 1.0 g (5.9 mmoles) of solid trimethylcyclopropenyl tetrafluoroborate was added. The reaction mixture was stirred at room temperature for 3 h. Solvent was then removed at 25°/40 mm. The residue was extracted with five 50 ml portions of pentane and solvent removed from the filtered pentane extracts at 25°/40 mm. Slow sublimation of the residue at 30°/0.5 mm gave a sublimate consisting of a mixture of orange crystals and yellow crystals. The orange crystals were $Hg[Co(CO)_4]_2$ and the yellow crystals were $(CH_3)_3C_3COCo(CO)_3$. These were separated mechanically and each product resublimed under the same conditions. Any impurities as recognized by crystals of the wrong color were then removed mechanically and the sublimations repeated further. After four such sequences of sublimation and mechanical separation 0.05 g (2.5% yield) of yellow crystalline $(CH_3)_3C_3COCo(CO)_3$, m.p. 80°, was obtained (Found: C, 47.9; H, 3.6; Co, 23.1; O, 25.2. $C_{10}H_9CoO_4$ calcd.: C, 47.6; H, 3.6; Co, 23.3; O, 25.4%.) The yield of orange $Hg[Co(CO)_4]_2$ was 0.04 g (2.5%).

IR spectrum (Perkin–Elmer Model 621 Spectrometer; grating optics)

CS_2 solution. $\nu(CO)$ frequencies at 2080 s, 2025 s, 2011 s, and 1719 s cm^{-1}.

KBr pellet. $\nu(CH)$ frequencies at 2980 w, 2960 w, 2920 m, and 2856 w cm^{-1}; $\nu(CO)$ frequencies at 2078 vs, 2018 vs, 2004 vs, and 1712 vs cm^{-1}; other bands at 1488 m, 1450 m, 1430 m, 1403 w, 1378 m, 1370 w, 1363 vw, 1354 vw, 1308 m, 1107 m, 1020 s, 948 w, 932 w, 916 w, and 825 m cm^{-1}.

Proton NMR spectrum (Varian HA-100 Spectrometer; 100 MHz)

Singlet resonances at τ 7.94 and 8.31 of relative intensities 1/2 in CS_2 solution.

Mass spectrum (Perkin–Elmer–Hitachi RMU 6 Mass Spectrometer)

The following ions were observed in a spectrum taken at 70 eV on a sample introduced into a chamber at 210° (relative intensities in parentheses): $(CH_3)_6C_6(CO)_2^+$ (9), $(CH_3)_5C_6(CO)_2^+$ (5), $(CH_3)_4CH_2C_6(CO)_2^+$ (4), $(CH_3)_6C_6CO^+$ (7), $(CH_3)_3$-

$CH_2C_6(CO)_2^+$ (5), $(CH_3)_5C_6CO^+$ (7), $(CH_3)_6C_6^+$ (53), $(CH_3)_5C_6^+$ (100), $C_9H_{11}^+$ (13), $(CH_3)_3C_3(CO)H^+$ (25), $C_7H_8O^+$ (15), $C_8H_9^+$? (11), $C_7H_7^+$ (14), $C_4H_7CO^+$ (8), $C_6H_{10}^+$ or $C_4H_6CO^+$ (12), $C_6H_9^+$ or $C_4H_5CO^+$ (12), $C_6H_8^+$ (8), $C_6H_7^+$ (16), $C_6H_5^+$ (15), $C_5H_7^+$ (58), $C_4H_6^+$ (72), $C_4H_5^+$ (44), $C_3H_5^+$ (39), $C_3H_3^+$ (36).

DISCUSSION

The reaction between trimethylcyclopropenyl tetrafluoroborate and $NaCo(CO)_4$ gave the following two cobalt carbonyl products: (1) the mercury derivative $Hg[Co(CO)_4]_2$ often[5] obtained as a by-product from reactions of $NaCo(CO)_4$ prepared with sodium amalgam; (2) the yellow compound $(CH_3)_3C_3COCo(CO)_3$ shown by its ν(CO) frequencies (2080, 2025, 2011, and 1719 cm^{-1}) to be the permethyl analogue of Coffey's[2] compound $(C_6H_5)_3C_3COCo(CO)_3$ [ν(CO) reported by Coffey[2]: 2080, 2015, and 1710 cm^{-1}]. The compound $(CH_3)_3COCo(CO)_3$ was a yellow very volatile solid which could be handled for at least short periods in air without decomposition but which decomposed readily in many solvents. However, solutions in carbon disulfide were reasonably stable as demonstrated by no change in the IR ν(CO) frequencies after 1 h in carbon disulfide solution.

The proton NMR spectrum of $(CH_3)_3C_3COCo(CO)_3$ suggested strongly the formulation as the keto-π-cyclobutenyl derivative (I) ($R = CH_3$) rather than the cyclopropenylcarbonyl derivative (II) ($R = CH_3$). Two methyl resonances of relative intensities 1/2 were observed in accord with the presence of two equivalent methyl groups and a third unique methyl group. The unique methyl group occurred at τ 7.94 which is in the region for methyl groups bonded to sp^2 carbon atoms but about 1 ppm too low for a methyl group bonded to an sp^3 carbon atom[6]. This is in accord with the keto-π-cyclobutenyl structure (I) ($R = CH_3$) which has the unique methyl group bonded to an sp^2 carbon atom but in discord with the cyclopropenylcarbonyl structure (II) ($R = CH_3$) which has the unique methyl group bonded to an sp^3 carbon atom.

Other spectroscopic properties of $(CH_3)_3C_3COCo(CO)_3$ are in accord with its formulation as the keto-π-cyclobutenyl derivative. The mass spectrum failed to exhibit a molecular ion even at temperatures as low as 50°. Instead the highest *m/e* ion was $(CH_3)_6C_6(CO)_2^+$ (*m/e* 218) formed by coupling of two of the keto-π-cyclobutenyl groups which would be obtained by cleavage of the cobalt–ring bonds. Fragmentation of this ion appeared to occur by loss of CO or CH_3; the base peak was $(CH_3)_5C_6^+$. A major ion in the mass spectrum (*m/e* 110) was $(CH_3)_3C_3(CO)H^+$ presumably formed by protolysis of the cobalt–ring bond. The formation of the R–R derivative in the mass spectrum of an $RCo(CO)_n$ derivative may be a characteristic feature of such mass spectra. Thus the mass spectrum of the trimethyltin derivative $(CH_3)_3SnCo(CO)_4$ run under similar conditions to those used in this work exhibited no molecular ion but instead the ion $(CH_3)_6Sn_2^+$ formed by the coupling of two trimethyltin groups[7].

The IR spectrum of $(CH_3)_3C_3COCo(CO)_3$ besides demonstrating its close relationship to Coffey's $(C_6H_5)_3C_3COCo(CO)_3$[2] also supported the keto-π-cyclobutenyl structure (I) ($R = CH_3$). The ν(CO) frequency at 1719 cm^{-1} is too high for the ν(CO) frequency of an acyl group bonded directly to a transition metal which appears around 1600 cm^{-1} [*e.g.* the acyl ν(CO) frequency in $CF_3COMn(CO)_5$

appears at 1625 cm^{-1}][8]. However, the ν(CO) frequency of 1719 cm^{-1} in $(CH_3)_3C_3COCo(CO)_3$ occurs at about 65 cm^{-1} below the ν(CO) frequency of cyclobutanone. This shift is roughly comparable to the 74 cm^{-1} downward shift of the ν(CO) frequency of tetraphenylcyclopentadienone (1716 cm^{-1}) in complexing with an iron tricarbonyl group to form $(C_6H_5)_4C_4COFe(CO)_3$ [ν(CO) 1642 cm^{-1}][9]. Unfortunately, an exact comparison of this type would require use of the ν(CO) frequency of the keto-π-cyclobutenyl radical rather than cyclobutanone; however, the ν(CO) frequency of the keto-π-cyclobutenyl radical is unobtainable by normal methods owing to the instability of such organic free radicals. However, available data on ν(CO) frequencies of organic ketones[10] suggests that the presence of the carbonyl group in a relatively strained four-membered ring affects the ν(CO) frequency much more than the presence of unsaturation in the ring.

The $(C_6H_5)_3C_3COCo(CO)_3$ studied by Coffey[2] exhibited two terminal ν(CO) frequencies at 2080 and 2015 cm^{-1} apparently corresponding to the A_1 and E modes of a *trans*-$L_3M(CO)_3$ system[11] with the keto-π-cyclobutenyl ligand formally occupying all three coordination positions of the L groups. However, the IR spectrum of the permethyl derivative $(CH_3)_3C_3COCo(CO)_3$, run under much higher resolution conditions than in the work of Coffey[2], exhibits *three* terminal ν(CO) frequencies (2080, 2025, and 2011 cm^{-1}). The splitting of the E mode in $(CH_3)_3C_3COCo(CO)_3$ suggests a *trans*-$L_2L'M(CO)_3$ rather than a *trans*-$L_3M(CO)_3$ system consistent with the low symmetry of the keto-π-cyclobutenyl ligand at least relative to the C_3 axis of the $Co(CO)_3$ group.

The NMR, IR, and mass spectral data thus all suggest keto-π-cyclobutenyl structures for the $R_3C_3COCo(CO)_3$ derivatives obtained from $Co(CO)_4^-$ and cyclopropenyl salts. The similarities in the IR spectra of $(C_6H_5)_3C_3COCo(CO)_3$ and $(C_6H_5)_3C_3COFe(CO)_2NO$[2] suggest a similar keto-π-cyclobutenyl structure for the iron dicarbonyl nitrosyl derivative. This can be reconciled with the degradation of $(C_6H_5)_3C_3COFe(CO)_2NO$ with 1,3-diphenylallyl chloride to give triphenylcyclopropenyl chloride on the basis of the observed tendency for small ring compounds with a carbonyl group in the ring (*i.e.* diarylcyclopropenones) to undergo a ring contraction reaction by loss of the carbonyl group as free carbon monoxide. Thus diarylcyclopropenones readily lose carbon monoxide to give diarylacetylenes[12]. In a similar manner the keto-π-cyclobutenyl cation initially formed by reaction of $(C_6H_5)_3C_3COFe(CO)_2NO$ with 1,3-diphenylallyl chloride could readily lose its carbonyl group to give the corresponding cyclopropenyl cation; the $4n+2$ aromatic stabilization of the cyclopropenyl cation would facilitate this decarbonylation reaction possibly causing it to occur at room temperature.

The keto-π-cyclobutenyl ligand apparently present in the $R_3C_3COCo(CO)_3$ derivatives [(I), $R=CH_3$ or C_6H_5] is the second known example of a ring of sp^2 carbon atoms containing one carbonyl group which bonds to a transition metal by using all of the sp^2 carbon atoms except the carbon atom of the carbonyl group. The first such system is cyclopentadienone which forms iron tricarbonyl derivatives of the type $R_4C_4COFe(CO)_3$[9] which, in a crude sense, may be regarded as being isoelectronic with the cobalt derivatives $R_3C_3COCo(CO)_3$. Another possible ligand of this type is the unknown keto-π-cyclohexadienyl system which may form manganese carbonyl complexes of the type $R_5C_5COMn(CO)_3$. Tropone[13] and cyclopropenone[14] are also potential ligands of this type, but the preparation of strictly analogous derivatives has been unsuccessful apparently because of the difficulty in bonding completely the positively charged three-membered and seven-membered unsaturated ring systems to transition metals.

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