13–18 for the $VOCl_4 \cdot H_2O^{2-}$ ion are $N_{\pi_2}{}^2 = 0.981$, $N_{\sigma_2}{}^2 = 0.582$, and $N_{\pi_1}{}^2 = 0.988$. The calculations were carried out with aid of a desk calculator.

U_p is evaluated as 0.177 from the nqr data at 33° using an average of the two frequencies. The MO parameters based on esr data give a value of 0.167.

This treatment could allow the estimation of the nqr frequencies for the equatorial chlorines in other oxyhalides for which molecular orbital parameters are available. Table IV lists the parameters for the $MoOCl_5^{2-}$ and $CrOCl_5^{2-}$ ions. These lead to predicted ^{35}Cl resonance frequencies of 3.20 and 8.91 MHz, respectively. Extensive searching between 2 and 15 MHz at room temperature and −140° has been unsuccessful to date in locating the resonances for the cesium salts of both ions.

TABLE IV

BONDING PARAMETERS FOR $MoOCl_5^{2-}$ AND $CrOCl_5^{2-}$

	$MoOCl_5^{2-}$ [a]	$CrOCl_5^{2-}$ [b]		$MoOCl_5^{2-}$ [a]	$CrOCl_5^{2-}$ [b]
$N_{\pi_2}{}^2$	0.905	0.886	S_{b_2}	0.12	0.12
$N_{\sigma_2}{}^2$	0.754	0.592	S_{b_1}	0.12	0.16
$N_{\pi_2}{}^2$	0.901	0.958	S_e	0.20	0.20

[a] Reference 2a. [b] Reference 1.

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1-Methyl-1-hydroxy(trimethylenemethane)cobalt Tricarbonyl Cation and Its Derivatives

BY SEI OTSUKA* AND AKIRA NAKAMURA

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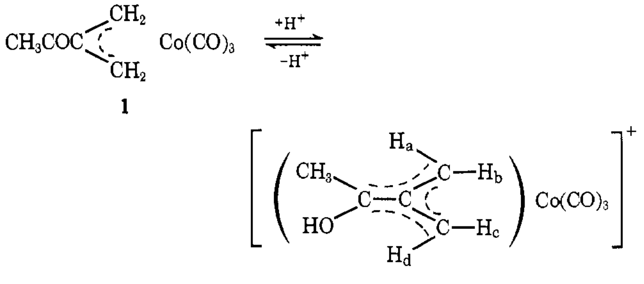
Metal complexes of trimethylenemethane, an interesting 4π-electron system, have been limited mainly to iron carbonyl derivatives.[1-6] We found protonation of 2-acetyl-π-allylcobalt tricarbonyl (1) leads to a novel, cationic trimethylenemethanecobalt system (2).



1

2

2-Acetyl-π-allylcobalt tricarbonyl [^1H nmr in C_6H_6: δ 1.76 (2 H), 1.89 (3 H), and 3.41 (2 H) ppm] was dissolved in concentrated sulfuric acid with a drastic change in its nmr spectrum giving rise to well-defined signals which are best interpreted in terms of the expected 1-methyl-1-hydroxytrimethylenemethane complex (2). Thus, two broad doublets at δ 3.72 and 2.85[7] ppm (J = 3 Hz) are assigned[8] to two nonequivalent mutually coupled protons, H_a and H_d, and two singlets at δ 2.81 and 2.53 are assigned to H_b and H_c protons. The highest field signal (sharp singlet, 3 H, δ 1.75 ppm) is then ascribed to CH_3 protons. Upon dilution with a small amount of water, only three singlets appeared at δ 2.60, 1.85, and 1.75 ppm (each with half-height width of 8 Hz). The singlet at δ 2.60 is apparently due to an averaging between protons, H_a and H_d, and also the singlet at δ 1.85 to that between H_b and H_c. The averaging appears to be accounted for in terms of a rapid equilibrium between the protonated and the deprotonated species. Recovery of the starting material on dilution with a large amount of water indicated deprotonation without skeletal change. Further evidence of the protonation was obtained by the comparison of the electronic spectra of 2-acetyl-π-allylcobalt tricarbonyl and its derivatives in ethanol and in concentrated sulfuric acid.

The result is shown in Table I for positions of absorption maxima only. Blue shift occurred with decrease in intensity when protonated with concentrated sulfuric acid. The formation of a positively charged species 2 was also confirmed by the ir CO stretching pattern in concentrated sulfuric acid. Thus, the solution placed between thin polyethylene films showed two strong bands at 2125 and 2084 cm^{-1}. The high-frequency shift from the unprotonated complex (*cf.* $\nu_{C\equiv O}$ at 2045 and 1983 cm^{-1}) is consistent with the formation of a cationic complex 2. The ketonic carbonyl region was covered with heavy absorption of sulfuric acid to inhibit a reliable conclusion. Attempts to isolate the protonated species 2 (a) by addition of concentrated aqueous $NaBF_4$ into a sulfuric acid solution of 1 or (b) by introduction of dry hydrogen chloride into a hexane solution of 1 have failed. Also attempts to alkylate 1 with trimethyloxonium[9] or triphenylmethyl tetrafluoroborate have been fruitless. It is worth noting that the ketone carbonyl frequencies of unprotonated 1 (1669 cm^{-1}) and of the benzoyl derivative (1650 cm^{-1}) rule out any significant bonding between cobalt and the carbonyl carbon before protonation.

TABLE I

COMPARISON OF ELECTRONIC SPECTRA FOR $CH_3COC_3H_4Co(CO)_2L$

	Absorption max, nm	
	In ethanol (ε)	In concd sulfuric acid
CO	353 (3.34 × 10^3)	307
	305 sh	380 sh
PPh_3	379 (2.45 × 10^3)	300 sh
	305 sh	
tert-BuNC	377 (4.18 × 10^3)	365 sh
	298	

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[7] This peak is partly overlapped with the δ 2.81 singlet.

[8] The assignment may be exchanged. The long-range coupling *via* a W-shaped route has been observed in (trimethylenemethane)iron complexes.[3,4]

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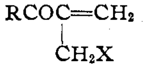
The starting material 1 is conveniently prepared from allene and acetylcobalt tetracarbonyl. A similar insertion reaction was observed for benzoylcobalt tetracarbonyl; 2-benzoyl-π-allyltricarbonylcobalt was obtained in a good yield. Preparation of 2-acyl-π-allyl complexes through a conventional route would

$$CH_3COCo(CO)_4 + C_3H_4 \longrightarrow 1$$

require a very unstable halovinyl ketone



$$\begin{matrix} RCOC{=}CH_2 \\ | \\ CH_2X \end{matrix}$$

as the starting material. Thus the novel insertion reaction provides a new simple route for the preparation of 2-substituted π-allyl derivatives.

Introduction of an electron-attracting acyl group into the π-allyl moiety appears to improve the air stability of π-allylcobalt tricarbonyl system. Further, the 2-acetyl-π-allyl group does not undergo an insertion reaction with isocyanide or CO; the reaction with *tert*-BuNC or PPh_3 merely results in substitution of one of the CO groups. Addition of a large excess of gaseous allene into the benzene solution of 1 at room temperature leads to the effective catalytic polymerization of allene into a regular 1,2 polymer.

$$2 + L \longrightarrow (CH_3COC_3H_4)Co(CO)_2L + CO$$

Experimental Section

Materials and Instruments.—Dicobalt octacarbonyl[10] and sodium tetracarbonylcobaltate[11] were prepared by the standard methods. Allene (Matheson Co.; purity *ca.* 98.7%) was used without purification. The ^1H nmr spectra were measured by a Jeol JNM 4H-100 instrument using TMS as internal standard. The ir and electronic spectra were obtained by Hitachi Perkin-Elmer 225 and Hitachi EPS-3T instruments. All reactions involving organometallic compounds were carried out under nitrogen.

2-Acetyl-π-allylcobalt Tricarbonyl (1).—Into a tetrahydrofuran solution (40 ml) of sodium tetracarbonylcobaltate freshly prepared from dicobalt octacarbonyl (1.4 g, 4.9 mmol) was added a tetrahydrofuran solution (10 ml) of acetyl chloride (0.75 ml, 8 mmol) at −10° and the mixture was stirred for 2 hr. Then 195 cm^3 of gaseous allene (8.1 mmol at 20°) was slowly introduced by a syringe into the yellowish brown solution at −15° during a 1-hr period. The mixture was allowed to stand overnight at −20°, filtered, and concentrated. Distillation gave an orange liquid (0.66 g, 32%, mp −20°) boiling at 55–56° (1 mm). Ether may be employed equally well as the solvent. *Anal.* Calcd for $C_8H_7O_4Co$: C, 42.49; H, 3.10. Found: C, 42.56; H, 3.14. Ir spectrum (Nujol mull) (cm^{-1}): 3080 (vw), 3000 (w), 2920 (w), 2045 (vs), 1983 (vs), 1668 (s), 1450 (m), 1413 (m), 1360 (s), 1335 (s), 1143 (s), 1005 (m), 975 (m), 960 (m), 940 (w), 808 (w), 770 (w), 660 (m). ^1H nmr spectrum (in the order of the solvent, chemical shifts in δ (ppm) from TMS, multiplicity, area, and assignment throughout this paper): $CDCl_3$, 2.31, singlet, 5H, CH_3 and anti protons; 3.65, singlet, 2H, syn protons.

2-Benzoyl-π-allylcobalt Tricarbonyl.—Addition of an ether solution (10 ml) of benzoyl chloride (0.9 ml, 7.6 mmol) into a stirred ether solution (100 ml) of sodium tetracarbonylcobaltate (1.4 g, 7.2 mmol) at 0° was followed by introduction of gaseous allene (300 cm^3, 12.5 mmol) at −78° in a manner similar to that described above. The reaction mixture was slowly warmed up to room temperature. The raw product obtained on evaporation of the solvent was purified by repeated distillations at 130° (6 mm) on a small scale to give a deep orange liquid (0.1 g, 22%). *Anal.* Calcd for $C_{13}H_9O_4Co$: C, 54.11; H, 3.13. Found: C, 54.04; H, 3.62. Ir spectrum (neat liquid) (cm^{-1}): 3070 (w), 2075 (vs), 2000 (vs), 1650 (s), 1598 (w), 1450 (s), 1355 (s), 1218 (s), 1015 (m), 990 (m), 735 (m), 700 (m), 625 (s). ^1H nmr spectrum (in $CDCl_3$): 2.42, singlet, 2H, anti protons; 3.62, singlet, 2H, syn protons; 7.43–7.74, multiplets, 5H, phenyl protons.

Reactions of 2-Acetyl-π-allylcobalt Tricarbonyl.—(a) Protonation readily occurred simply by dissolution of 1 into concentrated sulfuric acid or 48% fluoroboric acid. The solution was stable in air at room temperature for a few hours. (b) Substitution by triphenylphosphine occurred slowly at room temperature in benzene. The formation of $CH_3COC_3H_4Co(CO)_2(PPh_3)$ was confirmed by the appearance of ir bands at 2000 and 1950 cm^{-1} and also by the ^1H nmr spectrum in CS_2: 1.46, doublet (J_{HP} = 6 Hz), 2H, anti protons; 1.90, singlet, 3H, methyl; 2.92 (J_{HP} = 2.5 Hz), 2H, syn protons; 7.2, broad multiplets, 30H, phenyl protons. (c) Substitution by *tert*-butyl isocyanide occurred slowly at room temperature in benzene to give $CH_3COC_3H_4Co(CO)_2$(*tert*-BuNC). The raw product had ir bands at 2100 cm^{-1} (ν_{NC}), 1995 cm^{-1} (ν_{CO}), and 1950 cm^{-1} (ν_{CO}). The ^1H nmr spectrum (in CS_2) was consistent with the structure: 1.43, singlet, 9H, *tert*-Bu; 1.75, singlet, 2H, anti protons; 2.07, singlet, 3H, CH_3; 2.93, singlet, 2H, syn protons.

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Kinetics and Equilibria of Structural Interconversions. II. Cobalt(II) Bromide–Pyridine–Nitromethane

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A kinetic examination of octahedral–tetrahedral equilibrium in the cobalt(II) bromide–pyridine–nitromethane system has been carried out as part of a continuing study of the effects of ligands and solvents on the structural interconversions of cobalt(II) halide complexes in organic solvents.[2] Ligand properties can influence the coordination number of metal ions and much work has been directed toward evaluating their role in affecting the relative stabilities of octahedral and tetrahedral complexes of cobalt(II) halides.[3-5]

Experimental Section

Materials.—$Co(py)_2Br_2$ was the source of cobalt(II) and was prepared from cobalt(II) bromide hexahydrate[6] and pyridine by established techniques.[7] The visible spectrum of $Co(py)_2Br_2$ in nitrobenzene was in agreement with that obtained by other workers.[7] Pyridine and nitromethane were Spectroquality solvents from Allied Chemicals and Matheson Colemen and Bell, respectively. Eastman Chemicals tetraethylammonium perchlorate and tetrabutylammonium bromide were used with the latter salt further purified by recrystallization from ethyl acetate and anhydrous benzene. Both salts were dried under vacuum at 100° for 2 hr before use. The water content of 0.1 M solutions of Et_4NClO_4 and/or Bu_4NBr in pyridine and nitromethane did not exceed 0.014 and 0.033 M, respectively, as determined by the Karl Fischer method.

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