Reactions of π-Cyclo-octenyl-π-cyclo-octa-1,5-dienecobalt

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π-Cyclo-octenyl-π-cyclo-octa-1,5-dienecobalt, $Co(C_8H_{13})(C\text{-}H_{12})$, was treated with CO in pentane at −60° to −80° to give an orange monocarbonyl complex, $Co(CO)(C_8H_{13})(C_8H_{12})$. From this were derived phosphine or phosphite complexes, $Co(CO)(C_8H_{13})L_2$ [L = PPh_3, $PMePh_2$, $P(OPh)_3$] and hydridocarbonylphosphine complexes, $Co(H)(CO)L_3$. All these new complexes are diamagnetic, soluble in organic solvents, and show well defined proton n.m.r. and i.r. spectra on which structural assignments are based.

RECENTLY π-cyclo-octenyl-π-cyclo-octa-1,5-dienecobalt, $Co(C_8H_{13})(C_8H_{12})$, has been obtained by direct interaction of cyclo-octa-1,5-diene (cod) with $CoCl_2$ in the presence of metallic sodium.[1] Remarkable mobility of hydrogen atoms in the π-cyclo-octenyl ligand was observed in some chemical reactions, *e.g.*, release of cyclo-octene upon thermal decomposition or formation of $CoH(dp)_2$ [dp = 1,2-bis(diphenylphosphino)ethane]. The chemical property, which has been interpreted in terms of the molecular structure,[1] stimulated further studies on the chemical reactions.

Below −60° in solution $Co(C_8H_{13})(C_8H_{12})$ absorbs 1 mol. of carbon monoxide affording a thermally unstable carbonyl complex, $Co(CO)(C_8H_{13})(C_8H_{12})$ from which are derived several new types of complexes including hydridocarbonylphosphine complexes, $CoH(CO)L_3$ (L = PPh_3 and $PMePh_2$), carbonyl-(π-cyclo-octenyl)phosphine complexes, $Co(CO)(C_8H_{13})L_2$ [L = PPh_3, $PMePh_2$, and $P(OPh)_3$], etc. In this paper preparative reactions of these complexes and their structural assignments will be described.

EXPERIMENTAL

Solvents were used after dehydration and distillation under a nitrogen atmosphere. All manipulation was carried out under pure nitrogen atmosphere. Melting points were determined in capillary sealed under vacuum. I.r. spectra were measured by a Hitachi Perkin-Elmer model 225 and n.m.r. spectra by a 100 Mc. JNM 4H-100 of J.E.O.L. using Me_4Si as external reference.

*π-Cyclo-octenyl-π-cyclo-octa-*1,5-*dienecarbonylcobalt.*—Carbon monoxide was bubbled through a solution of $Co(C_8H_{13})(C_8H_{12})$ (1·1 g.) in 50 ml. of n-pentane between −80° and −60° for 1 min. The resultant yellow solution was filtered, concentrated under reduced pressure at low temperature (−40°/0·01 mm.), and cooled to −80°. The compound separated as orange needles (0·8 g.), m.p. 46—47° (decomp.) (Found: C, 67·05; H, 8·25. $C_{17}H_{25}CoO$ requires C, 67·3; H, 8·3%).

π-Cyclo-octenylcarbonylbis(triphenylphosphine)cobalt.—Triphenylphosphine (0·9 g., 3·44 mmoles) was added to a solution of $Co(CO)(C_8H_{13})(C_8H_{12})$ (0·27 g., 0·89 mmole) in toluene (5 ml.) at −20° and the resultant solution was warmed to 10°. By adding n-pentane dark brown crystals separated (0·6 g.), m.p. 106—108° (decomp.) (Found: C, 75·95; H, 5·9%; *M*, 752. $C_{45}H_{43}CoOP_2$ requires C, 75·0; H, 6·0%; *M*, 720·1). The molecular weight was determined cryoscopically in benzene.

π-Cyclo-octenylcarbonylbis(methyldiphenylphosphine)cobalt.—Methyldiphenylphosphine (0·68 g., 3·4 mmoles) was added to a solution of $Co(CO)(C_8H_{13})(C_8H_{12})$ (0·26 g., 0·86 mmole) in n-pentane (10 ml.) at −20° and the resultant solution was warmed to 10°. By standing dark red crystals separated (0·5 g.), m.p. 116—117° (decomp.) (Found: C, 70·5; H, 6·6. $C_{35}H_{39}CoOP_2$ requires C, 70·45; H, 6·6%).

π-Cyclo-octenylcarbonylbis(triphenyl phosphite)cobalt.—Triphenyl phosphite (1·18 g., 3·8 mmoles) was added to a

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[1] S. Otsuka and M. Rossi, *J. Chem. Soc.* (*A*), 1968, 2630.

solution of $Co(CO)(C_8H_{13})(C_8H_{12})$ (0·29 g., 0·95 mmole) in toluene (3 ml.) at −20° and the resultant solution was warmed to 25°. Addition of methanol produced a yellow oil; after removal of the solvents, the oil was treated with a small amount of methanol to give an orange microcrystalline product, m.p. 90—95° (decomp. ∼120°) (Found: C, 65·2; H, 5·25. $C_{45}H_{43}CoO_7P_2$ requires C, 66·2; H, 5·3%).

Hydridocarbonyltris(triphenylphosphine)cobalt(I).—(*a*) Triphenylphosphine (1·0 g., 3·92 mmoles) was added to a solution of $Co(CO)(C_8H_{13})(C_8H_{12})$ (0·3 g., 0·99 mmole) in toluene (5 ml.) at −20°, and the resultant solution was heated to 50° for 1 min. By adding n-pentane and cooling at 5°, orange prisms separated (0·66 g.), m.p. 172—173° (decomp.) (Found C, 76·1; H, 5·6; O, 1·6. $C_{55}H_{46}CoOP_3$ requires C, 75·5; H, 5·3; O, 1·85%).

(*b*) A solution of $Co(CO)(C_8H_{13})(PPh_3)_2$ (0·4 g.) and PPh_3 (0·3 g.) was warmed at 50—60° for 2 min. and the resultant yellow solution was treated with n-pentane to give a yellow powder. This product showed carbonyl stretching bands at 1907vs, 1916sh, and 1965m cm.$^{-1}$, different from those of the pure hydridocarbonyl complex described in (*a*). The analytical data (C, 74·5; H, 5·5; O, 4·15%) suggested contamination by other compounds containing more carbonyl groups. However, careful recrystallisation from benzene gave orange needles identical with those of (*a*).

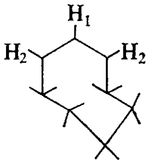

TABLE 1

Proton magnetic resonance for the cobalt complexes[a]

	H-1	Rel. intensity	H-2	Rel. intensity	–CH=	Rel. intensity	CH_2	Rel. intensity
$Co(CO)(C_8H_{13})(C_8H_{12})$ …………… ($C_6D_5CD_3$ soln., 0°)	6·0(t)	1	2·8(m)	2	3·7(m) 3·2(m)	2 2	2·5(m) 2·0(m) 1·6(m) 1·3(m)	2 6 4 6
$CO(CO)(C_8H_{13})(PPh_3)_2$ …………	4·5(m)	1	3·4(m)	2			2·3(m) 1·4(m)	4 6
$Co(CO)(C_8H_{13})(PMePh_2)_2$ ………	4·6(m)	1	3·1(m)	2			2·1(m) ∼1·3(—)	∼4 ∼6
$Co(CO)(C_8H_{13})[P(OPh)_3]_2$ ………	4·7(m)	1	4·0(m)	2			1·8(m) 1·3(m)	4 6
			δ (Co–H)		*J* (P–H)			
$CoH(CO)(PPh_3)_3$ ………………… (THF soln., 22°)		−13[b]	(q)	50	(Hz)			
$CoH(CO)(PMePh_2)_3$ ……………… (THF soln., 22°)		—13·5[b]	(q)	50	(Hz)			

[a] Measured in C_6D_6 at 22° unless otherwise noted. δ values from external $MeSi_4$ reference. Multiplicities are indicated in parentheses, t = triplet, q = quartet, and m = multiplet. Phosphine absorptions are omitted. [b] Negative sign indicates higher field from Me_4Si. [c] Complex triplet.

Hydridocarbonyltris(methyldiphenylphosphine)cobalt(I).—(*a*) Methyldiphenylphosphine (0·64 g., 3·2 mmoles) was added to a solution of $Co(CO)(C_8H_{13})(C_8H_{12})$ (0·28 g., 0·92 mmole) in toluene (5 ml.) at −20°, and the resultant dark red solution was heated until it became yellow-red. By adding n-pentane and cooling at −30°, orange-yellow crystals separated (0·5 g.). The product was washed with cold methanol and dried under vacuum, m.p. 114—115° (decomp.) (Found: C, 70·1; H, 6·1. $C_{40}H_{40}CoOP_3$ requires C, 69·75; H, 5·85%).

(*b*) A solution of $Co(CO)(C_8H_{13})(PMePh_2)_2$ (0·4 g.) and $PMePh_2$ (0·14 g.) in toluene (5 ml.) was heated at 70—80° for 3 min. to give a yellow-red solution. The solution was concentrated under reduced pressure, treated with n-pentane, and cooled at −80°, to give yellow crystals identical with those of (*a*).

Reaction of $[CoH(CO)(PPh_3)]_3$ *and Carbon Tetrachloride.*—The complex (0·2 g.) was treated with CCl_4 (0·3 ml.) at room temperature, and after a few minutes the solvent was distilled off under reduced pressure and collected in a Dry Ice trap. Chloroform was detected in the distilled solvent by means of the i.r. spectrum, using carbon tetrachloride as reference.

RESULTS AND UISCUSSION

*π-Cyclo-octenyl-π-cyclo-octa-*1,5-*dienecarbonylcobalt*, $Co(CO)(C_8H_{13})(C_8H_{12})$.—This compound was obtained by the reaction of $Co(C_8H_{13})(C_8H_{13})$ with carbon monoxide at low temperature (below −60°) with a short reaction time (*ca.* 1 min.). It forms diamagnetic orange needles very sensitive to oxygen and thermally unstable; the solids decomposed at about 46° under vacuum and the solution deteriorated under a nitrogen atmosphere below room temperature. The compound may be regarded as a fairly labile complex; it reacts readily with a variety of donor ligands. The reactions with phosphine or phosphite will be described below. From the n.m.r. spectrum the presence of π-co-ordinated cyclo-octentyl and cyclo-octa-1,5-diene ligands is evident. The whole spectrum (Table 1) more or less resembles that of the parent complex, $Co(C_8H_{13})(C_8H_{12})$, except that it lacks the high-field resonance (δ 0·4 p.p.m.) characteristic to the parent complex. The i.r. spectrum (Nujol mull) shows a carbonyl stretching band at 1956 cm.$^{-1}$ (Table 2) which is close to that of the isoelectronic monocarbonyl complex, of formula $Fe(CO)(C_5H_5)(\pi\text{-}C_3H_5)$.[2]

In comparison with the closely related $Fe(CO)(C_5H_5)(\pi\text{-}C_3H_5)$ [2] or $[Co(CO)(C_5H_5)(\pi\text{-}C_3H_5)]X$ [3] the complex, $Co(CO)(C_8H_{13})(C_8H_{12})$, is not thermally stable. A brief study on the thermal decomposition was made

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[2] M. L. H. Green and P. L. I. Nagy, *J. Chem. Soc.*, 1963, 189.

[3] E. O. Fischer and R. D. Fischer, *Z. Naturforsch.*, 1961, **16**b, 475.

TABLE 2

I.r. spectra of the cobalt complexes in the 2200—1600 cm.$^{-1}$ region

Compound	ν (cm.$^{-1}$)
$Co(CO)(C_8H_{13})(C_8H_{12})$ [a]	1956vs
$Co(CO)(C_8H_{13})(PPh_3)_2$ [a]	1897vs
$Co(CO)(C_8H_{13})(PMePh_2)_2$ [a]	1877vs
$Co(CO)(C_8H_{13})[P(OPh)_3]_2$ [a]	1935vs
$CoH(CO)(PPh_3)_3$ [a]	1901vs, 2013w
$CoH(CO)(PMePh_2)_3$ [a]	1886vs, 1918w, 1943w
$CoH(CO)(PPh_3)_3$ [b]	1903vs, 1943m

[a] Nujol mull between NaCl discs. [b] Benzene solution in 0·1 mm. NaCl cells.

by following the i.r. spectral change of a Nujol mulled sample which was heated from 10° to 60°. The results were as follows. (1) Firstly the intensity at 1956 cm.$^{-1}$ decreased and then disappeared. (2) New bands appeared at 1972sh, 1980s, 2017m, and 2050m cm.$^{-1}$. (3) Finally at 50—60° the bands at 1972 and 2017 cm.$^{-1}$ disappeared leaving only two bands at 1980vs and 2056s cm.$^{-1}$. An orange-coloured unstable liquid complex showing the above carbonyl stretching bands was isolated from the thermal decomposition carried out separately. Although the instability prevented a good analytical result, the liquid compound is deduced to be π-cyclo-octenyltricarbonylcobalt, $Co(CO)_3(C_8H_{13})$, on the basis of the observatious that the same compound is produced by treating $Co(C_8H_{13})(C_8H_{12})$ with an excess carbon monoxide at room temperature and that the carbonyl stretching pattern resembles the spectra of π-allyl or substituted π-allyl complexes containing a $Co(CO)_3$ moiety, *e.g.*, π-cycloheptatrienyl-tricarbonylcobalt [4] (2050 and 1970 cm.$^{-1}$) and 1,3-dialkyl-π-allyltricarbonylcobalt [5] (2000—1960 cm.$^{-1}$). The formula $Co(CO)_3(C_8H_{13})$ receives further support from its reactions with maleic anhydride giving rise to $Co(CO)_2(C_4H_2O_3)(C_8H_{13})$ which will be described separately.

π-Cyclo-octenylcarbonylbis(phosphine)cobalt, $Co(CO)(C_8H_{13})(PR_3)_2$.—These complexes were obtained when the reaction of $Co(CO)(C_8H_{13})(C_8H_{12})$ with an excess of phosphine or phosphite was carried out at low temperature (10°). The bis(triphenylphosphine)complex obtained in the form of dark brown plates is soluble in aromatic solvents and sparingly soluble in methanol. It is moderately stable to air in solid state, but the solution is sensitive to air; in the absence of oxygen the solution was stable indefinitely at room temperature. The methyldiphenylphosphine complex obtained as dark red plates is less stable to air than the corresponding triphenylphosphine derivative. The triphenyl phosphite complex was obtained as an orange compound very soluble in most organic solvents. One carbonyl stretching band occurred in each of these three complexes; the wavenumber decreases with increase in the electron-donating property of the ligands (Table 2), *i.e.*, $Co(CO)(C_8H_{13})[P(OPh)_3]_2$ (1935) > $Co(CO)(C_8H_{13})(PPh_3)_2$ (1897) > $Co(CO)(C_8H_{13})(PMePh_2)_2$ (1877 cm.$^{-1}$). The n.m.r. spectra (Table 1) indicate the presence of π-cyclo-octenyl ligand but the lowest-field resonance ($\delta \sim 4·6$ p.p.m.), which is assignable to the central allylic proton H-1 (see the numbering in Table 2), is no longer triplet; instead it is a complex triplet owing to the couplings with two phosphine or phosphite ligands. It may be worthwhile to note that the chemical shift of H-1 appears to be rather insensitive to the nature of the phosphine ligands whereas the resonance for the terminal allylic protons H-2 shifts upfield with increase in the electron-donating property of the ligand; *i.e.*, $P(OPh)_3$ (δ 4·0) > PPh_3 (δ 3·4) > PCH_3Ph_2 (δ 3·1).

Although cobalt complexes of a general formula $Co(\pi\text{-allyl})(CO)_n(PR_3)_{3-n}$ where $n = 3$ and 2 have been known,[6] examples for compounds having $n = 1$ were so far unknown. The monocarbonylbis(phosphine)-π-cyclo-octenylcobalt complexes are also labile being susceptible to a variety of substitution reactions. Substitution of the π-cyclo-octenyl ligand with phosphine results in a ready hydrogen transfer from the ligand to metal giving rise to hydrido-complexes as described below.

Hydridocarbonyltris(phosphine)cobalt, $CoH(CO)(PR_3)_3$.—The hydrido-complexes of formula, $CoH(CO)(PPh_3)_3$ and $CoH(CO)(PMePh_2)_3$ have been obtained either by the direct reaction of $Co(CO)(C_8H_{13})(C_8H_{12})$ with 4 or more mol. of phosphine at higher temperature (50—70°) or by heating the solution of $Co(CO)(C_8H_{13})(PR_3)_2$ in the presence of free phosphine. The orange prisms of the hydridotriphenylphosphine complex are moderately soluble in benzene and tetrahydrofuran and very stable to air in the solid state. Recently Uchida *et al.*[7] reported briefly the formation of a hydrido-complex having the same formula by treating the nitrogen hydrido-complex, $CoH(N_2)(PPh_3)_3$, with carbon monoxide. The yellow hydridomethyldiphenylphosphine complex is very soluble in aromatic solvents and easily decomposed by air. Attempts to obtain the corresponding hydridophosphite complex by heating the toluene solution of $Co(CO)(C_8H_{13})[P(OPh)_3]_2$ in the presence of free phosphite were unsuccessful.

The i.r. spectra in the carbonyl and metal–hydrogen stretching regions are in Table 2. The very strong band of 1901 cm.$^{-1}$ (Nujol) or 1903 cm.$^{-1}$ (in benzene) for $CoH(CO)(PPh_3)_3$ is undoubtedly the carbonyl stretching absorption. In view of the metal–hydrogen stretching frequencies, 2004 and 2068 cm.$^{-1}$ found for $RhH(CO)(PPh_3)_3$ and $IrH(CO)(PPh_3)_3$,[8] respectively, the weak band at 2013 cm.$^{-1}$ appears to be due to ν_{M-H}. However, in solution the higher-frequency band disappeared and a medium intensity band appeared at 1943 cm.$^{-1}$. The complex, $CoH(CO)(PMePh_2)_3$, showed two weak bands at 1918 and 1943 cm.$^{-1}$, unassignable at present, in addition to the strong carbonyl band at

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[4] R. B. King and M. B. Bisnette, *Inorg. Chem.*, 1964, **3**, 785.

[5] I. A. Bertrand, H. B. Jonassen, and D. W. Moore, *Inorg. Chem.*, 1963, **2**, 601.

[6] R. G. Guy and B. L. Shaw, *Adv. Inorg. Chem. Radiochem.*, 1962, **4**, 112.

[7] A. Misono, Y. Uchida, M. Hidai, and T. Kuse, *Chem. Comm.*, 1968, 981.

[8] S. S. Bath and L. Vaska, *J. Amer. Chem. Soc.*, 1963, **85**, 3500.

1886 cm.$^{-1}$. This stretching frequency (1886 cm.$^{-1}$) seems quite low for a terminal carbonyl group. However, the difference (15 cm.$^{-1}$) in the frequencies (1901 and 1886 cm.$^{-1}$) for the two hydridocarbonyl complexes is reasonable in view of the difference in donor properties of PPh_3 and $PMePh_2$.

The n.m.r. spectra are listed in Table 1. Because of the low solubility of $CoH(CO)(PPh_3)_3$, it was difficult to detect the signal due to the hydride nucleus. By raising the sensitivity of a 100 Mc. instrument, we were finally able to locate the quartet resonance centered at δ -13 p.p.m. (approximately τ 23). In the case of $CoH(CO)(PMePh_2)_3$, owing to the enhanced solubility, the high-field resonance of the hydride nucleus was readily observed as a 1 : 3 : 3 : 1 quartet with $J_{P-H} = 50$ Hz arising from the coupling with three equivalent phosphorus nuclei, the chemical shift and/or the coupling constant being comparable to those found in $CoH(CO)_4$,[9] $CoH(CO)_3PPh_3$,[10] $CoH(CO)_2(PPh_3)_2$,[10] $RhH(CO)(PPh_3)_3$,[8] and in good agreement with the reported values[7] (δ 12 p.p.m. J_{P-H} 48 Hz) for $CoH(CO)(PPh_3)_3$. The n.m.r. spectra suggest the stereochemistry to be trigonal bipyramid with three equatorial phosphine ligands, which has been established by *X*-ray analysis for $RhH(CO)(PPh_3)_3$[11] and for $CoH(N_2)(PPh_3)_3$.[12]

The finding of $CoH(CO)(PR_3)_3$ completes a series of hydridocarbonylphosphine complexes $CoH(CO)_n(PR_3)_{4-n}$ ($n = 4$—0). Therefore it will be of interest to compare the thermal stabilities and protonic or hydridic characters of hydrogen ligand of the series. The thermal stability may be qualitativety estimated from the decomposition points which follow: $CoH(CO)_4$ ($-20°$) $<$ $CoH(CO)_3PPh_3$ (20°) $<$ $CoH(CO)_2(PPh_3)_2$ (140°) $<$ $CoH(CO)(PPh_3)_3$ (172°). Thus introduction of phosphine ligand(s) raises the stability. The acidic property of hydrogen ligand decreases in the order of $CoH(CO)_4 >$ $CoH(CO)_3PPh_3 > CoH(CO)_2(PPh_3)_2$ [10,13] and the basic behaviour of $CoH(dp)_2$ was established by Sacco *et al.*[14] We would then predict that $CoH(CO)(PPh_3)_3$ will be in between $CoH(CO)_2(PPh_3)_2$ and $CoH(dp)_2$.

It is to be noted that the chemical reactions of $Co(C_8H_{13})(C_8H_{12})$ and $Co(CO)(C_8H_{13})(C_8H_{12})$ we have investigated indicate their versatility in preparative chemistry for low-valent cobalt complexes.

We thank the Japan Society for the Promotion of Science for the fellowship granted to M. R. during 1968.

[8/1352 *Received, September* 16*th*, 1968]

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[9] R. A. Friedel, I. Wender, S. L. Shufler, and H. W. Sternberg, *J. Amer. Chem. Soc.*, 1955, **77**, 3951.

[10] W. Hieber and H. Duchatsch, *Chem. Ber.*, 1965, **98**, 2933.

[11] S. J. La Placa and J. A. Ibers, *J. Amer. Chem. Soc.*, 1963, **85**, 3501.

[12] J. H. Enemark, B. R. Davis, J. A. McGinnety, and J. A. Ibers, *Chem. Comm.*, 1968, **2**, 96.

[13] W. Hieber and E. Lindner, *Chem. Ber.*, 1961, **94**, 1417.

[14] A. Sacco and R. Ugo, *J. Chem. Soc.*, 1964, 3274.