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(CYCLOPROPYLCARBONYL)METAL COMPLEXES

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SUMMARY

The preparation of remarkably stable cyclopropylcarbonyl complexes of manganese, rhenium, iron and iridium is described. Attempts to prepare σ-cyclopropyl complexes by decarbonylation reactions were not successful, little reaction occurring under most conditions described. Reaction between PPh_3 and the manganese complex resulted in concomitant decarbonylation and ring-opening to give a π-allyl derivative, π-$C_3H_5Mn(CO)_3PPh_3$.

INTRODUCTION

Although many complexes of transition metals containing σ-bonded alkyl or aryl groups, or their fluorinated analogues, are known[1], no reports of any complexes containing cyclopropyl groups have appeared. The reaction of cyclopropane with H_2PtCl_6 in acetic anhydride gives a brown complex[2,3], recently shown[4] to have an analogous structure to the tetrameric platinum alkyls, and containing a C_3Pt ring. The crystal structure of a pyridine derivative, $[(C_3H_6)PtPy_2Cl_2]$, has been reported[5], and contains a similar four-membered ring. Other transformations of the latter giving an ylid complex, $[(C_3H_6)PtPy_2Cl_4]$, were described. More recently, the reaction between cyclopropane and $[Rh(CO)_2Cl]_2$ was shown to afford a C_4Rh ring with carbon monoxide incorporated[6]. Extensive investigations of palladium chloride complexes with vinyl-[7-10] and methylene-cyclopropanes[11] have shown that π-allylpalladium complexes are formed, apparently by ring-opening reactions of postulated 'edge' complexes[12]. With iron carbonyls, substituted diene–iron tricarbonyl complexes are formed with substituted cyclopropylstyrenes[13] and spiro[2.4]hepta-4,6-diene[14], whereas methylenecyclopropane gives trimethylenemethane–iron tricarbonyl[15].

These unusual and interesting reactions of cyclopropane and its derivatives prompted us to attempt the synthesis of σ-cyclopropyl–metal compounds, to further examine the various transformations of this three-membered ring. A possible route to such complexes is decarbonylation of the corresponding acyl–metal compounds.

RESULTS AND DISCUSSION

(σ-Cyclopropylcarbonyl)metal derivatives were easily obtained by reaction of the carbonylmetal anions $[Mn(CO)_5]^-$, $[Re(CO)_5]^-$ and $[\pi$-$C_5H_5Fe(CO)_2]^-$ with cyclopropanecarboxylic acid chloride. The manganese (I) and rhenium (II) complexes formed very volatile, airstable, white needle-like crystals with a camphoraceous odour, which sublimed easily at normal pressures. The iron complex, (III), is an orange-yellow oil, which could be distilled, with little decomposition, at ~140° (0.1 mm), and which remained liquid on a −78° probe. This large liquid range is unusual for this type of complex. The iron derivative slowly decomposed in air and light at room temperature, but was stable under nitrogen. All these complexes were soluble in hydrocarbons and other common organic solvents.

Complexes (I), (II) and (III) proved to be extremely stable, and experiments to decarbonylate these complexes were generally unsuccessful. No decarbonylation of the manganese complex occurred on heating in a sealed tube at 60° for 12 h, nor on UV irradiation in light petroleum for a similar period. A small amount of carbonyl-free decomposition product was sometimes obtained, but the majority of complex (I) was recovered unchanged. Heating at 65° for 12 h in light petroleum in a sealed tube gave only a small amount of $Mn_2(CO)_{10}$ in addition to the recovered complex; stronger heating (120°/24 h) gave much brown solid, and some $Mn_2(CO)_{10}$ was again isolated from the filtrate. Also present, and identified spectroscopically, was a small amount of π-$C_3H_5Mn(CO)_4$.

The iron complex (III) was not decarbonylated under the following conditions: (a) heating at 120° for 24 h in light petroleum in a sealed tube; (b) UV irradiation of a light petroleum solution for 24 h in a sealed tube, or of the complex alone for 16 h.

The use of $(Ph_3P)_3RhCl$ to abstract carbon monoxide from a variety of organic compounds has been described[16]. Reaction of this complex with the (cyclopropylcarbonyl)manganese, -rhenium and -iron complexes gave up to 50% of the expected $(Ph_3P)_2Rh(CO)Cl$, but other products were not satisfactorily characterised, possibly due to formation of intractable triphenylphosphine-substituted complexes. Recently, the use of this reagent to decarbonylate complexes of iron has been described[17].

However, decarbonylation and ring-opening occurs on reaction of complex (I) with triphenylphosphine, when the bright yellow π-allyl derivative, π-$C_3H_5Mn(CO)_3PPh_3$ (IV) is formed. This complex, which has not been described previously, was identified by comparison with an authentic sample prepared from π-allylmanganese tetracarbonyl and triphenylphosphine and fully characterised by the usual methods. The reaction between cyclopropanecarboxylic acid chloride and the anion $[Mn(CO)_4PPh_3]^-$ gave *cis*-(cyclo-$C_3H_5CO)Mn(CO)_4PPh_3$ (V).

The iron complex (III) does not react with triphenylphosphine on heating, but irradiation in cyclohexane for nearly 60 h gave yellow $C_3H_5COFe(CO)(PPh_3)(\pi$-$C_5H_5)$ (VI). This formed an airstable, involatile solid, showing only one terminal $\nu(CO)$ band, together with the expected acyl $\nu(CO)$ absorption. A small amount of triphenylphosphine oxide was also isolated from this reaction.

The reaction of the acid chloride with $Pt(PPh_3)_4$ gave *cis*-$(Ph_3P)_2PtCl_2$ as the only isolable product. With the complex $(Ph_3P)_2Ir(CO)Cl$, reaction with the acid chloride occurred rapidly in benzene solution to give a white solid. Filtration and recrystallisation from dichloromethane/light petroleum mixtures gave white crystals of $(Ph_3P)_2Ir(CO)Cl_2(COC_3H_5)$ (VII). The single terminal $\nu(CO)$ absorption was found at 2068 cm^{-1}, and the acyl $\nu(CO)$ at 1612 cm^{-1}. As discussed below, the proton NMR spectrum showed bands in similar positions to those for complexes (I)–(III), and the IR spectrum also exhibited characteristic bands for the cyclopropyl group at

2930 and 2860 cm^{-1}. From this, we conclude that oxidative addition of the acid chloride has occurred without rearrangement to give the cyclopropylcarbonyl complex.

Spectroscopic studies

The IR spectral bands of the complexes are given in Table 1. In the carbonyl region, the spectra of complexes (I) and (II) showed the expected five bands for the $M(CO)_5$ group; that of complex (III) showed two bands of equal intensity, characteristic of the π-$C_5H_5Fe(CO)_2$ group. The acyl band occurred between 1600–1640 cm^{-1}, compared with a value of 1776 cm^{-1} in the acid chloride. Complex (IV) showed three sharp ν(CO) bands, indicating C_s symmetry for the metal carbonyl group. The IR spectrum of complex (V) indicated that the *cis* isomer was formed, in contrast to reactions of this anion with fluorocarbons[18], but similarly to the reaction with iodomethane[19]. Complex (VI) showed only one ν(CO) band, at 1922 cm^{-1}, and the acyl carbonyl band occurred at 1602 cm^{-1}.

The proton NMR spectra (Table 2) of the cyclopropyl complexes are similar, showing resonances assigned to H_A and H_B at τ 8.45–9.15 and 9.20–9.45 (complex multiplets), and to H_C at τ 7.40–7.60 (triplet of triplets). First-order coupling to H_C was apparent, but the intensities were insufficient for complete analysis of the spectrum. Complex (IV) exhibited a typical allyl spectrum, with three signals at τ 6.28 (complex multiplet), 7.96 (double quartet) and 8.36 (double quartet).

The mass spectra of complexes (I), (II) and (III) showed the expected stepwise loss of the metal carbonyl and acyl carbonyl groups, to give ions of the type $C_3H_5M^+$, which underwent further fragmentation.

The relative stabilities of complexes (I), (II) and (III) are surprising. Their

TABLE 1

INFRARED SPECTRA OF SOME COMPLEXES (CM^{-1})

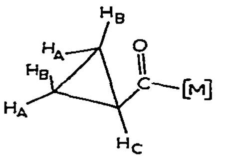
Complex	ν(CO)	Other bands
(I)	2105 m, 2040 m, 2010 vs, 2002 s, 1973 w^{a}	3007 vw, 1638 m, 1337 m, 1191 m, 1097 vw, 1060 vw, 1034 m, 945 s, 829 m, 792 vw, 649 (br) vs^{b}
(II)	2130 w, 2060 w, 2045 w, 2016 vs, 1999 s, 1976 w, 1956 vw^{a}	3010 vw, 1606 m, 1337 m, 1192 m, 1034 m, 955 ms, 832 w, 687 w, 674 m, 637 w^{b}
(III)	2023 vs, 1958 vs^{a}	1654 m, 1639 m, 1470 w, 1350 w, 1173 w, 1060 w, 983 m, 848 m^{a}
(IV)	2000 vs, 1930 vs, 1905 vs^{a}	3150 vw, 3080 (sh), 3062 m, 3030 w, 3008 w, 1334 vw, 1312 w, 1205 s, 1187 m, 1162 w, 1122 s, 1095 s, 1073 w, 1033 m, 1003 m, 915 m, 752 s, 730 s, 702 vs, 682 s, 630 s^{b}
(V)	2030 w, 1945 vs, 1916 s^{b}	3050 m, 2915 w, 1602 m, 1188 w, 1090 m, 1030 vw, 1000 vw, 748 ms, 700 s, 670 m, 640 m^{b}
(VI)	1922 vs^{a}	1602 m, 1090 w, 940 m, 817 m, 743 m, 722 s, 697 s, 667 s^{a}
(VII)	2068 vs^{c}	2960 w, 2930 m, 2860 w, 1612 ms, 1485 w, 1437 m, 1379 w, 1342 vw, 1195 vw, 1095 w, 1040 w, 1006 vw, 966 w, 755 w, 703 m^{c,d}

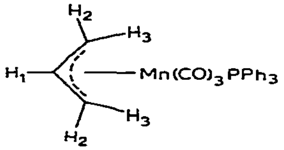
[a] Cyclohexane. [b] CS_2. [c] Nujol. [d] Hexachlorobutadiene.

TABLE 2

PROTON NMR DATA FOR SOME COMPLEXES[a]

(I) M = $Mn(CO)_5$
(II) M = $Re(CO)_5$
(III) M = $Fe(CO)_2(\pi\text{-}C_5H_5)$
(VII) M = $Ir(CO)Cl_2(PPh_3)_2$





(IV)

Complex	Chemical shift (τ)[b]	Assignment	Coupling constants (Hz)
(I)	7.54 tt	H_C	J_{AC}, J_{BC}: 4.8, 7.4
	8.99 m	H_B	
	9.32 m	H_A	
(II)	7.63 tt	H_C	J_{AC}, J_{BC}: 4.6, 7.6
	9.13 m	H_B	
	9.47 m	H_A	
(III)	5.28 s	C_5H_5	
	7.62 tt	H_C	J_{AC}, J_{BC}: 4.7, 7.5
	9.14 m	H_B	
	9.47 m	H_A	
(IV)	2.74 m	$P\text{-}C_6H_5$	Not determined
	6.28 m	H_1	
	7.96 dq	H_2	
	8.36 dq	H_3	
(VII)	7.38 tt	H_C	Not determined
	8.46 m	H_B	
	9.20 m	H_A	
cyclo-C_3H_5COCl	7.99 m	H_C	Not determined
	8.75 m	H_B	
	8.91 m	H_A	

[a] All in CS_2 except complex (VII) ($CDCl_3$). [b] dq, double quartet; m, complex multiplet; s, sharp singlet; tt, triplet of triplets.

resistance to decarbonylation suggests some interaction between the cyclopropyl group and the acyl carbonyl function, preventing migration of the former onto the metal. Recent NMR[20], electron diffraction[21], and solvolysis studies[22] have indicated that some conjugative interaction of a cyclopropane ring with an adjacent unsaturated group can occur.

Under conditions where migration can occur, *e.g.* extensive pyrolysis, or in the reaction of complex (I) with triphenylphosphine, ring opening occurs, presumably under the influence of the metal. Orbital symmetry arguments predict[23] that the ring opening of the cyclopropyl cation should be a disrotatory process, whereas with the corresponding radical or anion, the conrotatory mode is favoured. These two processes cannot be distinguished in the present case, but experiments using appropriately substituted cyclopropane derivatives should resolve this point.

EXPERIMENTAL

IR spectra were recorded on a Perkin–Elmer 257 double-beam spectrophotometer. PMR spectra were obtained with a Varian Associates HA100 spectrometer at 100 MHz. Mass spectra were taken using an AEI MS9 double-focussing spectrometer, operating at 70 eV ionising energy.

Solvents were dried and redistilled before use. Chromatography was on columns packed with Florisil, initially in light petroleum (boiling range 40–60°). All reactions were run under nitrogen.

Analytical and m.p. data are collected in Table 3.

TABLE 3

ANALYTICAL DATA

Complex	M.p. (°C)	Found C(%)	Found H(%)	Found Mol.wt.[a]	Calcd. C(%)	Calcd. H(%)	Calcd. Mol.wt.
(I) $C_9H_5MnO_6$	79	40.50	2.09	264	40.90	1.89	264
(II) $C_9H_5O_6Re$	100–101	27.25	1.17	396	27.32	1.26	396
(III) $C_{11}H_{10}FeO_3$	Oil	53.05	4.33	246	53.65	4.07	246
(IV) $C_{24}H_{20}MnO_3P$[b]	140–142	65.30	4.70		65.12	4.52	
(V) $C_{26}H_{20}MnO_5P$[c]	167–169	62.29	4.27		62.53	4.02	
(VI) $C_{28}H_{25}FeO_2P$	161–163	69.08	5.24		70.00	5.21	
(VII) $C_{41}H_{35}Cl_2IrO_2P_2$[d]	220–221	55.01	4.05		55.65	3.96	

[a] Mass spectrometry. [b] Found: Mn, 11.93; P, 7.12. Calcd.: Mn, 12.44; P, 7.01%. [c] Found: P, 7.45. Calcd.: P, 6.22%. [d] Found: Cl, 8.03; O, 3.62; P, 7.00. Calcd.: Cl, 8.11; O, 3.68; P, 7.11%.

Reactions of cyclopropanecarboxylic acid chloride

(*a*) *With* $[Mn(CO)_5]^-$. A tetrahydrofuran solution of $Mn_2(CO)_{10}$ (1.95 g, 5 mmoles) was converted to the sodium derivative by stirring with 2% sodium amalgam for 3 h. After separation of the excess amalgam, cyclopropanecarbonyl chloride (1.0 g, 10 mmoles) in tetrahydrofuran (10 ml) was added dropwise. After stirring for 24 h at room temperature, solvent was removed to give a grey solid. Sublimation at 30° (0.01 mm) gave fine white needles of pure cyclo-$C_3H_5COMn(CO)_5$ (I) (2.47 g, 94%). The solid sublimes at 70–80° at normal pressures and can be obtained in long (~4 cm) fine needles, which have a camphorlike odour.

(*b*). *With* $[Re(CO)_5]^-$. The sodium derivative from $Re_2(CO)_{10}$ (326 mg, 0.5 mmole) in tetrahydrofuran (30 ml) reacted with the acid chloride (105 mg, 1 mmole) in the same solvent (5 ml) for 12 h at room temperature. Evaporation of the reaction mixture and sublimation of the residue at 40° (0.01 mm) gave white crystalline cyclo-$C_3H_5CORe(CO)_5$ (268 mg, 68%).

(*c*). *With* $[\pi\text{-}C_5H_5Fe(CO)_2]^-$. A similar reaction using the sodium salt from $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ (3.54 g, 10 mmoles) and cyclopropanecarbonyl chloride (2.1 g, 20 mmoles), after refluxing for 3 h gave a red semi-solid on removal of solvent from the filtered reaction mixture. This was extracted with dichloromethane (2 x 5 ml) and chromatographed. A bright orange-yellow oil was eluted with 9/1 light petroleum/benzene, and purified by vacuum distillation (bath temperature 140°/0.01 mm) to give pure cyclo-$C_3H_5COFe(CO)_2(\pi\text{-}C_5H_5)$ (III) (2.75 g, 56%). The oil is somewhat sensitive to light and air.

(*d*). *With* $[Mn(CO)_4PPh_3]^-$. A mixture of the acid chloride (150 mg, 1.4 mmoles) with the sodium salt from $[Mn(CO)_4PPh_3]_2$ (430 mg, 0.5 mmole) was stirred for 16 h at room temperature. After removal of solvent, chromatography gave a yellow band, eluted with benzene, which gave bright yellow crystals of cyclo-$C_3H_5COMn(CO)_4PPh_3$ (V) (115 mg, 26%) on evaporation. A second fraction, eluted with 9/1 benzene/ether, afforded an unidentified orange-yellow solid (35 mg), m.p. 191–193°. (Found: C, 49.6; H, 3.0; Mn, 8.4; P, 7.1%.)

(*e*). *With* $Pt(PPh_3)_4$. A mixture of the acid chloride (3.0 g, 29 mmoles) and $Pt(PPh_3)_4$ (3.0 g, 2.4 mmoles) in benzene (40 ml) was kept in a sealed tube for 24 h at room temperature. A white crystalline solid separated, and was filtered and washed with light petroleum to give *cis*-$(Ph_3P)_2PtCl_2$ (490 mg, 26%), m.p. 309–310° (lit.[3] 300–310°). (Found: C, 54.9; H, 4.1. $C_{36}H_{30}Cl_2P_2Pt$ calcd.: C, 54.7; H, 3.8%.) The far IR spectrum showed two bands at 319 ms and 296 ms cm^{-1} and was identical with that of an authentic sample.

(*f*). *With* $(Ph_3P)_2Ir(CO)Cl$. The acid chloride (234 mg, 2.3 mmoles) and $(Ph_3P)_2Ir(CO)Cl$ (234 mg, 0.3 mmole) in benzene (20 ml) were sealed in a Carius tube. After a few minutes at room temperature a white solid began to settle; the reaction appeared to be finished, with complete decolourisation of the solution, after 42 h. The solid was filtered to give a small amount (22 mg) of a white solid which was a mixture, and not investigated further. The filtrate was evaporated and recrystallised from a dichloromethane/light petroleum mixture to give white crystals of $(Ph_3P)_2Ir(CO)Cl_2(COC_3H_5)$ (VII) (55 mg, 20%).

Substitution reactions with triphenylphosphine

(*a*). *With cyclo*-$C_3H_5COMn(CO)_5$. The complex (100 mg, 0.4 mmole) and triphenylphosphine (100 mg, 0.4 mmole) in cyclohexane (35 ml) were refluxed for a total of 8 h after which time no further change in the carbonyl IR spectrum occurred. Removal of solvent and recrystallisation of the residue from light petroleum gave fine yellow crystals of π-$C_3H_5Mn(CO)_3PPh_3$ (IV) (85 mg, 48%), identified by comparison with a sample prepared as described below.

(*b*). *With cyclo*-$C_3H_5COFe(CO)_2(\pi$-$C_5H_5)$. A mixture of $C_3H_5COFe(CO)_2(\pi$-$C_5H_5)$ (246 mg, 1 mmole) and triphenylphosphine (262 mg 1 mmole) in cyclohexane (40 ml) was irradiated for 57 h, after which time the two original ν(CO) bands were replaced by a single new band. Removal of solvent followed by chromatography gave fine white needles of triphenylphosphine oxide, eluted with light petroleum (10 mg, 3.6%; m.p. and mixed m.p. 155–157°) and also identified from its mass spectrum, and an orange yellow fraction, eluted with a 1/1 light petroleum/ether mixture. Recrystallisation of this product from light petroleum/ether mixtures gave bright orange-yellow crystals of cyclo-$C_3H_5COFe(CO)(PPh_3)(\pi$-$C_5H_5)$ (VI) (142 mg, 30%).

Preparation of π-$C_3H_5Mn(CO)_3PPh_3$. A mixture of π-$C_3H_5Mn(CO)_4$ (ref. 24) (420 mg, 2 mmoles) and triphenylphosphine (525 mg, 2 mmoles) in cyclohexane (25 ml) was refluxed for 3 h. Evaporation gave an oily solid, which on recrystallisation from light petroleum (three times) gave bright yellow needles of π-$C_3H_5Mn(CO)_3PPh_3$ (IV) (130 mg, 15%).

Decarbonylation experiments

Only those experiments in which evidence of decarbonylation was obtained are described below.

(*a*). *Pyrolysis of* $C_3H_5COMn(CO)_5$. The complex (350 mg) in light petroleum (20 ml) was heated for 24 h at 120° in a sealed tube. An amount of brown solid was filtered off, and the yellow filtrate was evaporated. Sublimation gave $Mn_2(CO)_{10}$ (38 mg, 15%), identified spectroscopically. In addition to bands due to the original complex, and to $Mn_2(CO)_{10}$, the filtrate showed ν(CO) bands at 2073 m, 1996 (sh), 1980 vs, 1963 vs and 1933 w cm^{-1} [lit.[24] values for π-$C_3H_5Mn(CO)_4$: 2075 m, 1997 s, 1979 vs, 1964 vs and 1932 w cm^{-1}].

(*b*). *Reaction of $C_3H_5COMn(CO)_5$ with $(Ph_3P)_3RhCl$.* A mixture of the acyl complex (13 mg, 0.05 mmole) and $(Ph_3P)_3RhCl$ (30 mg, 0.03 mmole) in dichloromethane (6 ml) was stirred at room temperature for 16 h. During this time a yellow solid separated. Filtration gave $(Ph_3P)_2Rh(CO)Cl$, m.p. 201–203°. (lit.[25] m.p. 195–197°) identified spectroscopically [ν(CO), 1966 vs; lit.[25] value: 1970 vs cm^{-1}]. From the filtrate, a small amount of the original complex was isolated.

(*c*). *Reaction between $C_3H_5CORe(CO)_5$ and $(Ph_3P)_3RhCl$.* A similar reaction using $C_3H_5CORe(CO)_5$ (100 mg, 0.25 mmole) and $(Ph_3P)_3RhCl$ (231 mg, 0.25 mmole) in dichloromethane (10 ml) gave a yellow solid after only 1.75 h, identified as $(Ph_3P)_2Rh(CO)Cl$ (103 mg, 60%). (Found: C, 64.45; H, 4.10. $C_{37}H_{30}ClOP_2Rh$ calcd.: C, 64.33; H, 4.35%.)

(*d*). *Reaction between $C_3H_5COFe(CO)_2(\pi\text{-}C_5H_5)$ and $(Ph_3P)_3RhCl$.* The corresponding reaction using the iron complex (50 mg, 0.2 mmole) and $(Ph_3P)_3RhCl$ (185 mg, 0.2 mmole) in dichloromethane for 24 h gave yellow $(Ph_3P)_2Rh(CO)Cl$, together with a small amount (2 mg) of bright yellow crystals, m.p. 211°, showing a single ν(CO) band at 1974 s cm^{-1}.

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