Preparation, Structure, and Reactions of some New Complexes containing Copper or Silver Bonded to Various Transition Metals

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The complexes $[Me_4N][Ag\{M(CO)_3(cp)\}_2]$, $[Me_4N][Cu\{M(CO)_3(cp)\}_2]$, $[\{(cp)M(CO)_3Ag\}_n]$, $[\{(cp)M(CO)_3Cu(L)_x\}_n]$ [M = Cr, Mo, or W; $(L)_x = OH_2$ or $\frac{1}{2}OH_2\cdot\frac{1}{2}NH_3$; cp = η-cyclopentadienyl] $[\{Co(CO)_4Ag\}_n]$, $[\{Co(CO)_4Cu(L)_y\}_n]$, $[\{(Bu_3P)Co(CO)_3Ag\}_n]$, $[\{(Bu_3P)Co(CO)_3Cu\}_n]$, $[\{[(PhO)_3P]Fe(CO)_2(NO)Ag\}_n]$, $[\{HFe(CO)_4Ag\}_2]\cdot AgNO_3$, and $[V(CO)_6Cu(L{-}L)_2]$ (L–L = 1,10-phenanthroline or 2,2′-bipyridyl) are described, many for the first time, and their i.r. spectra reported. It is suggested that the neutral complexes are covalent oligomers with n = *ca.* 3 or 4 which tend to ionize in donor solvents. All the complexes form 1 : 1 adducts with L–L; many of these are ionic. Scission reactions with Ph_3SnCl, Ph_3PbCl, I_2, MeI, or mercury are described for the derivatives of Cr, Mo, or W. The salt $Na(C_5H_5)$ converts $[\{(cp)Mo(CO)_3Ag\}_n]$ to $[Ag\{Mo(CO)_3(cp)\}_2]^+$; $Et_2O\cdot BF_3$ reverses the reaction.

MOST compounds containing copper or silver bonded to a transition-metal carbonyl moiety also have phosphines or arsines co-ordinated to the Group 1B metal.[1] Some do not, *e.g.* $[Co(CO)_4Ag]$.[2,3] We describe here a number of neutral and anionic complexes of this type.

EXPERIMENTAL

All reactions were carried out in purified solvents under an atmosphere of nitrogen and at room temperature unless it is stated otherwise. Copper(I) chloride,[4] $[\{(Bu_3P)Co(CO)_3\}_2]$,[5] $[\{(PhO)_3P\}(OC)_2(ON)Fe]_2Hg$,[6] and $Na[M(CO)_3(cp)]$ (M = Cr, Mo, or W; cp = η-cyclopentadienyl) [7] were prepared as described.

Preparation of Covalent Complexes.—A solution of $Na[M(CO)_3(cp)]$ (10 mmol) in bis(2-methoxyethyl) ether (bme) (100 cm^3) and water (20 cm^3) was added rapidly to $AgNO_3$ (5 g) in water (150 cm^3) or to CuCl (4 g) in 5% aqueous ammonia (150 cm^3). The resulting suspension was extracted with dichloromethane and the extracts were washed with water, dried over magnesium sulphate, and ethanol (100 cm^3) added. The total volume was reduced to 150 cm^3. Yellow crystals of $[\{(cp)M(CO)_3Ag\}_n]$, $[\{(cp)Mo(CO)_3Cu\cdot\frac{1}{2}OH_2\cdot\frac{1}{2}NH_3\}_n]$, or $[\{(cp)W(CO)_3Cu\cdot OH_2\}_n]$ were filtered off, washed with pentane, and dried (yields *ca.* 50%). Attempts to prepare $[\{(cp)Cr(CO)_3Ag\}_n]$ failed, and solutions of $[\{(cp)Cr(CO)_3Cu\}_n]$ were used to prepare $[\{(cp)Cr(CO)_3Cu(phen)\}_n]$ (phen = 1,10-phenanthroline). The following yellow crystalline solids were obtained similarly in 30—70% yields: $[\{Co(CO)_4Ag\}_n]$; $[\{Co(CO)_4Cu(L)_y\}_n]$ [$(L)_y$ = indeterminate number of H_2O and NH_3 ligands]; $[\{(Bu_3P)Co(CO)_3Ag\}_n]$; $[\{(Bu_3P)Co(CO)_3Cu\}_n]$; and $[\{[(PhO)_3P]Fe(CO)_2(NO)Ag\}_n]$.

Aqueous $AgNO_3$ (9 g in 150 cm^3) was added slowly to a methanol solution (10 cm^3) of $Na[Fe(CO)_4H]$ prepared from $Fe(CO)_5$ (2·6 cm^3).[8] Acetone (200 cm^3) was added, and the filtered mixture reduced in volume. Light brown $[\{HFe(CO)_4Ag\}_2]\cdot AgNO_3$ was filtered off and dried (yield *ca.* 40%).

Preparation of Salts.—Solid CuCl (0·5 g) or aqueous $AgNO_3$ (0·85 g in 50 cm^3) was added to $Na[M(CO)_3(cp)]$ (10 mmol; M = Cr, Mo, or W) in bis(2-methoxyethyl) ether (100 cm^3)–water (20 cm^3). These mixtures were filtered, and $[Me_4N]Cl$ (2 g) in water (100 cm^3) added. Cream crystals of $[Me_4N][M'\{M(CO)_3(cp)\}_2]$ were filtered off, washed, and dried (M′ = Cu or Ag; yields 80—90%). Addition of water (20 cm^3) instead of $[Me_4N]Cl$ precipitated $[(bme)_2Na][Cu\{Mo(CO)_3(cp)\}_2]$. The salt $[Me_4N][Ag\{Mo(CO)_3(cp)\}\{W(CO)_3(cp)\}]$ was prepared from solid $[\{(cp)Mo(CO)_3Ag\}_n]$ (5 mmol) and an aqueous bis(2-methoxyethyl) ether solution of $Na[W(CO)_3(cp)]$ (5 mmol). The $[(bme)_2Na]^+$ and $[Me_4N]^+$ salts of $[Cu\{Mo(CO)_3(cp)\}\{W(CO)_3(cp)\}]^-$ were obtained similarly.

Reactions with Lewis Bases.—1,10-Phenanthroline monohydrate (phen·H_2O) (0·2 g) gave yellow-to-red insoluble 1 : 1 adducts in *ca.* 95% yield with 1 mmol of $[Me_4N][Cu\{M(CO)_3(cp)\}_2]$, $[\{(cp)M(CO)_3Ag\}_n]$, or $[\{(cp)M(CO)_3Cu(L)_x\}_n]$, but not $[Me_4N][Ag\{M(CO)_3(cp)\}_2]$, in tetrahydrofuran (thf) (50 cm^3). Similarly we obtained other 1 : 1 adducts of phen or 2,2′-bipyridyl (bipy) with the moieties $[Co(CO)_4Ag]$ and $[Co(CO)_4Cu]$ (orange in colour), $[(Bu_3P)Co(CO)_3Ag]$ (red), $[(Bu_3P)Co(CO)_3Cu]$ (black), and $[\{(PhO)_3P\}Fe(CO)_2(NO)Ag]$ (light brown). White $[\{(Bu_3P)Co(CO)_3Ag(dppe)\}_n]$ was also prepared [dppe = 1,2-bis(diphenylphosphino)ethane].

Triphenylphosphine (0·52 g) and $[Me_4N][Cu\{M(CO)_3(cp)\}_2]$ (1 mmol) in thf (40 cm^3) gave a precipitate of $[Me_4N][Mo(CO)_3(cp)]$ (yield 45% based on Mo), and, after the addition of light petroleum to the filtrate and cooling, yellow $[(Ph_3P)_4Cu][Cu\{M(CO)_3(cp)\}_2]$ (yield 70% based on Cu). The silver complexes did not react. Copper or silver precipitated on addition of $[\{(cp)Mo(CO)_3Ag\}_n]$ or $[\{(cp)Mo(CO)_3Cu\cdot\frac{1}{2}OH_2\cdot\frac{1}{2}NH_3\}_n]$ to sodium cyclopentadienide (5 mmol) in thf (40 cm^3). After dilution with water (10 cm^3) the solution was filtered, $[Me_4N]Cl$ (0·5 g) added, and $[Me_4N][M'\{Mo(CO)_3(cp)\}_2]$ obtained (yield 70% based on Mo; M′ = Cu or Ag). Addition of KCN (2 mmol) and $[Me_4N]Cl$ (1 mmol) to solutions of $[Me_4N][M'\{Mo(CO)_3(cp)\}_2]$ (1 mmol) in thf gave almost quantitative yields of $[Me_4N][Mo(CO)_3(cp)]$.

1,10-Phenanthroline (0·5 g) or bipy (0·4 g) in thf (20 cm^3) were added to mixtures of $[(bme)_2Na][V(CO)_6]$ (0·5 g) and CuCl (0·5 g) in bis(2-methoxyethyl) ether (20 cm^3)–5% aqueous ammonia (100 cm^3). The precipitates were recrystallized from thf to give brown crystalline $[\{V(CO)_6Cu(bipy)_2\}_n]$ or red $[\{V(CO)_6Cu(phen)_2\}_n]$ in 60—70% yields. Their silver analogues could not be obtained.

Reactions with Lewis Acids.—Pentane (20 cm^3) was added to a mixture of $Et_2O\cdot BF_3$ (0·5 cm^3) and $[Me_4N][Ag\{M(CO)_3(cp)\}_2]$ (1 mmol) (M = Mo or W) in thf (40 cm^3). Cooling to −20 °C gave crystalline $[\{(cp)M(CO)_3Ag\}_n]$ (yields *ca.* 60% based on Ag).

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M.p.s, analyses, and i.r. spectra (1 700—2 100 cm^{-1}) of complexes described in the text

Complex	M.p. [a] (θ_c/°C)	Analyses/%						Spectral solvent	I.r. spectra [b]
		Found			Calc.				
		C	H	N or P	C	H	N or P		
$[\{(cp)Mo(CO)_3Cu\cdot\frac{1}{2}OH_2\cdot\frac{1}{2}NH_3\}_n]$ [c]	140 (decomp.)	29·6	2·2	2·0	29·0	2·3	2·1	$CHCl_3$	1 843 (9·5), 1 878 (10), 1 960 (4·1), 1 978 (3·9)
								thf	1 776 (sh), 1 801 (9·5), 1 819 (10), 1 918 (10), 1 924 (sh)
$[\{(cp)Mo(CO)_3Ag\}_n]$ [d]	145 (decomp.)	27·6	1·7		27·3	1·4		$CHCl_3$	1 870 (9·0), 1 903 (10), 1 946 (9·9), 1 966 (sh)
								thf	1 792 (sh), 1 813 (3·5), 1 829 (3·8), 1 918 (5·3), 1 933 (2·9), 1 963 (sh), 1 967 (10), 2 046 (7·3)
$[\{(cp)W(CO)_3Cu\cdot OH_2\}_n]$	155 (decomp.)	22·2	1·7		23·0	1·7		$CHCl_3$	1 835 (9·0), 1 878 (10), 1 943 (5·5), 1 963 (5·5)
								thf	1 778 (sh), 1 799 (6·4), 1 817 (7·1), 1 919 (10), 1 938 (9·5)
$[\{(cp)W(CO)_3Ag\}_n]$	125 (decomp.)	21·9	0·8		21·8	1·1		$CHCl_3$	1 857 (9·0), 1 893 (9·5), 1 941 (10), 1 958 (sh)
								thf	1 786 (sh), 1 802 (3·5), 1 826 (4·4), 1 914 (10), 1 929 (4·4), 1 952 (6·5), 2 039 (4·6)
$[\{Co(CO)_4Cu(L)_x\}_n]$								CS_2	2 000 (10), 2 017 (3·1), 2 039 (3·4), 2 057 (3·6), 2 064 (10), 2 078 (1·3)
								Et_2O	1 883 (sh), 1 933 (10), 1 968 (7·9), 2 002 (2·0), 2 026 (4·4), 2 041 (4·5), 2 056 (1·4)
								thf	1 943 (10, br), 2 025 (4·2)
								py	1 885 (10)
$[\{Co(CO)_4Ag\}_n]$								CS_2	1 974 (5·6), 2 000 (3·9), 2 018 (5·2), 2 036 (1·6), 2 059 (10), 2 064 (sh)
								Et_2O	1 953 (7·9), 2 005 (10), 2 028 (5·5), 2 051 (3·8), 2 069 (7·6)
								thf	1 941 (10, br), 2 023 (4·9)
								py	1 886 (10), 1 933 (8·2), 1 968 (sh), 2 022 (2·8), 2 048 (10)
$[\{(Bu_3P)Co(CO)_3Cu\}_n]$	125—127 (d)	44·1	6·9		44·0	6·6		CS_2	1 889 (sh), 1 917 (10)
$[\{(Bu_3P)Co(CO)_3Ag\}_n]$		39·7	6·0	7·2	39·8	6·0	6·9	CS_2	1 903 (sh), 1 917 (10), 1 977 (2·1)
$[\{[(PhO)_3P]Fe(CO)_2(NO)Ag\}_n]$	123—124	42·3	2·4	2·3	42·9	2·8	2·5	CS_2	1 719 (7·1), 1 737 (5·2), 1 939 (10), 1 988 (4·7)
$[\{HFe(CO)_4Ag\}_2]\cdot AgNO_3$ [f]	120 (decomp.)	12·8	0·3	1·4	13·3	0·3	1·9	thf	1 905 (sh), 1 914 (2·3), 1 999 (10)
$[Me_4N][Cu\{Cr(CO)_3(cp)\}_2]$	160 (decomp.)	45·0	4·5	2·3	44·5	4·1	2·6	thf	1 776 (sh), 1 788 (8·9), 1 817 (10), 1 905 (9·1), 1 920 (9·1)
$[(Ph_3P)_4Cu][Cu\{Cr(CO)_3(cp)\}_2]$	162—164	66·8	4·3		66·9	4·4		thf	1 773 (sh), 1 794 (8·6), 1 817 (10), 1 907 (10), 1 920 (8·6)
$[Me_4N][Ag\{Cr(CO)_3(cp)\}_2]$	150 (decomp.)	41·1	3·7	2·2	41·2	3·8	2·4	thf	1 781 (sh), 1 803 (8·1), 1 824 (7·9), 1 910 (10), 1 933 (6·3)
$[Me_4N][Cu\{Mo(CO)_3(cp)\}_2]$	200 (decomp.)	38·0	3·7	2·4	37·6	3·5	2·2	thf	1 786 (sh), 1 802 (9·4), 1 818 (10), 1 910 (7·3), 1 926 (6·7)
$[(Ph_3P)_4Cu][Cu\{Mo(CO)_3(cp)\}_2]$	166—168	63·3	4·1	7·5	63·4	4·2	7·5	thf	1 771 (sh), 1 799 (8·3), 1 814 (10), 1 917 (9·3), 1 926 (4·6)
$[(bme)_2Na][Cu\{Mo(CO)_3(cp)\}_2]$	165 (decomp.)	39·2	5·0		39·8	4·5		thf	1 771 (sh), 1 799 (9·0), 1 824 (9·4), 1 918 (10), 1 926 (7·1)
$[Me_4N][Ag\{Mo(CO)_3(cp)\}_2]$	190 (decomp.)	35·2	3·5	2·2	35·7	3·3	2·1	thf	1 795 (sh), 1 812 (8·1), 1 829 (8·1), 1 917 (10), 1 933 (6·3)
$[Me_4N][Cu\{Mo(CO)_3(cp)\}\{W(CO)_2(cp)\}]$	135 (decomp.)	33·3	3·0	1·9	33·5	3·1	2·0	thf	1 779 (sh), 1 799 (9·1), 1 815 (10), 1 910 (8·0), 1 926 (7·2)
$[(bme)_2Na][Cu\{Mo(CO)_3(cp)\}\{W(CO)_3(cp)\}]$	130 (decomp.)	36·0	4·0		36·0	4·1		thf	1 780 (sh), 1 796 (9·2), 1 818 (10), 1 913 (8·4), 1 924 (6·7)
$[Me_4N][Ag\{Mo(CO)_3(cp)\}\{W(CO)_3(cp)\}]$	165 (decomp.)	31·3	2·9	1·5	31·6	2·9	1·8	thf	1 797 (sh), 1 815 (8·8), 1 824 (9·4), 1 913 (10), 1 929 (7·1)
$[Me_4N][Cu\{W(CO)_3(cp)\}_2]$	170 (decomp.)	30·2	2·9	1·7	30·0	2·7	1·7	thf	1 777 (sh), 1 794 (9·5), 1 811 (10), 1 907 (6·4), 1 920 (6·4)
$[(Ph_3P)_4Cu][Cu\{W(CO)_3(cp)\}_2]$	168—170	57·0	3·8	6·7	57·2	3·8	6·7	thf	1 763 (sh), 1 792(7·4), 1 808 (10), 1 911 (9·0), 1 919 (4·7)
$[Me_4N][Ag\{W(CO)_3(cp)\}_3]$	170 (decomp.)	27·8	2·5	1·6	28·3	2·6	1·7	thf	1 795 (sh), 1 805 (7·2), 1 823 (7·3), 1 911 (10), 1 926 (4·8)
$[\{(cp)Cr(CO)_3Cu(phen)\}_n]$		54·4	3·2	6·2	53·9	2·9	6·3	Nujol	1 752 (10), 1 786 (5·9), 1 888 (8·8)
$[\{(cp)Mo(CO)_3Cu(phen)\}_n]$		49·5	2·9	5·9	49·0	2·7	5·7	Nujol	1 757 (10), 1 790 (5·0), 1 893 (8·4)
$[\{(cp)Mo(CO)_3Ag(phen)\}_n]$		44·9	2·5	5·3	45·1	2·4	5·3	Nujol	1 774 (sh), 1 782 (10), 1 884 (7·1)
$[\{(cp)W(CO)_3Cu(phen)\}_n]$		39·0	2·4	4·8	41·6	2·3	4·9	Nujol	1 755 (10), 1 785 (7·0), 1 889 (8·9)
$[\{(cp)W(CO)_3Ag(phen)\}_n]$		39·4	2·2	4·3	38·7	2·1	4·5	Nujol	1 782 (10), 1 814 (8·6), 1 910 (7·6)
$[\{Co(CO)_4Cu(bipy)\}_n]$		42·5	1·8	7·2	43·0	2·0	7·2	Nujol	1 857 (3·3), 1 917 (sh), 1 926 (6·2), 1 938 (10), 2 020 (6·0)
$[\{Co(CO)_4Cu(phen)\}_n]$		45·6	2·1	6·6	46·3	1·9	6·8	Nujol	1 842 (6·0), 1 900 (7·3), 1 936 (10), 2 017 (7·3)
$[\{Co(CO)_4Ag(phen)\}_n]$		40·9	1·6	5·8	40·8	1·7	6·0	Nujol	1 903 (10), 1 924 (sh), 1 955 (7·7), 2 021 (6·9)
$[\{(Bu_3P)Co(CO)_3Cu(phen)\}_n]$	124—124	53·8	6·1	4·7	55·0	5·9	4·8	thf	1 807 (4·0), 1 874 (9·2), 1 943 (10), 1 957 (sh)
								thf–phen	1 806 (0·1), 1 875 (0·3), 1 943 (10), 1 958 (sh)
$[\{(Bu_3P)Co(CO)_3Ag(phen)\}_n]$	100 (decomp.)	51·7	5·3	4·4	51·2	5·3	4·4	thf	1 901 (sh), 1 918 (10), 1 972 (3·5)
								thf–phen	1 863 (sh), 1 877 (10), 1 899 (sh), 1 954 (3·5)
$[\{(Bu_3P)Co(CO)_3Ag(dppe)\}_n]$	105—106 (d)	57·9	6·0	10·6	58·0	5·8	10·9	CS_2	1 862 (sh), 1 881 (8·4), 1 917 (10), 1 975 (2·4)
$[\{[(PhO)_3P]Fe(CO)_2(NO)Ag(phen)\}_n]$	115—116 (d)	52·8	3·2	5·6	52·3	3·1	5·7	Nujol	1 692 (7·0), 1 708 (2·8), 1 852 (10), 1 911 (1·7), 1 940 (1·6)
$[V(CO)_6Cu(bipy)_2]$	148—149	51·1	2·9	8·8	52·5	2·7	9·4	$CHCl_3$	1 823 (sh), 1 853 (5·7), 1 887 (8·3), 1 935 (4·3), 1 958 (sh), 2 029 (10)
								thf	1 857 (10), 1 890 (2·3), 1 936 (0·1), 2 024 (0·2)
$[V(CO)_6Cu(phen)_2]$	188—189	57·3	2·7	8·6	56·0	2·5	8·7	$CHCl_3$	1 816 (sh), 1 851 (10), 1 878 (7·5), 1 936 (2·6), 1 960 (sh), 2 028 (5·7)
								thf	1 857 (10), 1 889 (2·3)
$[Me_4N][Cu(phen)\{Cr(CO)_3(cp)\}_2]$		52·6	4·1	5·6	53·3	4·2	5·8	Nujol	1 754 (10), 1 784 (6·7), 1 891 (7·1)
$[Me_4N][Cu(phen)\{Mo(CO)_3(cp)\}_2]$		46·7	3·9	5·3	47·5	3·7	5·2	Nujol	1 757 (10), 1 785 (6·9), 1 893 (7·9)
$[Me_4N][Cu(phen)\{W(CO)_3(cp)\}_2]$		39·1	3·0	4·0	39·0	3·1	4·2	Nujol	1 754 (10), 1 782 (4·6), 1 889 (7·9)

[a] Determined in sealed tubes. Decomp. = decomposed without melting and d = melted with decomposition. Where no figure is given, the sample decomposed at non-reproducible temperatures. [b] Absorption bands due to ν(NO) and ν(CO) vibrations. Peak positions (cm^{-1}) with relative peak heights in parentheses. thf–phen = Tetrahydrofuran with excess of 1,10-phenanthroline dissolved in it. sh = Shoulder and b = broad. [c] Cu, Found: 18·8. Calc.: 19·5%. [d] Ag, Found: 29·9. Calc.: 30·4%. [e] Ag, Found: 38·6. Calc.: 38·9%. [f] Ag, Found: 45·1. Calc.: 44·6%.

Cleavage Reactions.—Solutions of $[Me_4N][M'\{M(CO)_3(cp)\}_2]$ (1 mmol) and Ph_3SnCl, Ph_3PbCl, or I_2 (2 mmol) in thf gave, after 30 min, $[(cp)M(CO)_3SnPh_3]$, $[(cp)M(CO)_3PbPh_3]$, or $[(cp)M(CO)_3I]$ in 70—85% yields, whilst mercury (1 cm^3) converted them to $[\{(cp)M(CO)_3\}_2Hg]$ over 3—7 h. Methyl iodide and the silver salts afforded $[(cp)M(CO)_3Me]$ (50%) and $[(cp)M(CO)_3I]$ (10%) within 20 min, but their copper counterparts gave only $[(cp)M(CO)_3Me]$ after 7—10 h.

M.p.s, analyses, and i.r. spectra of the new complexes are summarized in the Table. Spectra were obtained as described previously.[9]

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[9] J. Newman and A. R. Manning, *J.C.S. Dalton*, 1973, 1593.

RESULTS AND DISCUSSION

The covalent compounds are very light and air sensitive but the $[Me_4N][M'\{M(CO)_3(cp)\}_2]$ salts (M = Cr, Mo, or W; M′ = Cu or Ag) are more resistant to oxidation. The $[Me_4N][M'\{M(CO)_3(cp)\}_2]$ derivatives are insoluble in non-polar solvents, and their solutions (0·01M) in thf or pyridine (py) have high conductivities. Typical conductivities, κ (S cm^{-1}), are (M = Mo and M′ = Cu) $6{\cdot}5 \times 10^{-5}$ in thf and $34{\cdot}0 \times 10^{-5}$ in py, and (M = W and M′ = Ag) $4{\cdot}0 \times 10^{-5}$ (thf) and $28{\cdot}5 \times 10^{-5}$ (py).

Similarities between the i.r. spectra of the $[Ag\{M(CO)_3(cp)\}_2]^-$ salts and their neutral $[\{(cp)M(CO)_3\}_2Hg]$ analogues [10] imply that the two series are isostructural with linear M–Ag–M or M–Hg–M systems (*cf.* ref. 10). The lower ν(CO) frequencies of the silver anions are attributed to their negative charge. This is also true for their copper counterparts, but the two series have different spectra. This may be due to (*a*) non-linear co-ordination about the copper atom (*cf.* ref. 11), (*b*) conformers having different orientations of the $(cp)M(CO)_3$ moieties, or (*c*) interactions of the anions with cations or solvent. The changes in the ν(CO) i.r. spectrum of $[Cu\{Mo(CO)_3(cp)\}_2]^-$ with cation point to (*c*), whilst its resemblance to that of $[\{(cp)(OC)_3Mo\}_2SnCl_2]$ [12] indicates (*a*).

Solutions of $[\{(cp)M(CO)_3Ag\}_n]$, $[\{LCu(CO)_3Ag\}_n]$, and $[\{[(PhO)_3P]Fe(CO)_2(NO)Ag\}_n]$ (M = Mo or W; L = CO or Bu_3P), or their copper counterparts, in carbon disulphide and chloroform are non-conducting. The frequencies of their ν(CO) or ν(NO) vibrations also indicate that these complexes are covalent. As their i.r. spectra are invariably too complicated for monomeric species * (*cf.* $[(cp)Mo(CO)_3(SnPh_3)]$,[13] $[LCo(CO)_3(SnPh_3)]$,[14] or $[\{(PhO)_3P\}Fe(CO)_2(NO)(SnCl_3)]$ [15]), we formulate them as covalent oligomers. The molecular weight of the most stable, $[\{(Bu_3P)Co(CO)_3Ag\}_n]$, was 1 580 in benzene and 1 260 in chloroform; calculated values are 1 356 ($n = 3$) and 1 808 ($n = 4$). The differences between the spectra of the copper and silver derivatives may be due to (*a*)—(*c*) mentioned previously, or (*d*) to different degrees of oligomerization. The presence of H_2O or NH_3 ligands, strongly bonded to copper rather than the other metal atoms and absent from the silver complexes, suggests that (*a*) is important here.

I.r. spectra of thf or pyridine solutions of $[\{(cp)Mo(CO)_3Cu{\cdot}\tfrac{1}{2}OH_2{\cdot}\tfrac{1}{2}NH_3\}_n]$ and $[\{(cp)W(CO)_3Cu{\cdot}OH_2\}_n]$ show that the $[Cu\{M(CO)_3(cp)\}_2]^-$ anions are the only carbonyl-containing species present. Differences between these spectra and those of authentic samples of $[Me_4N][Cu\{M(CO)_3(cp)\}_2]$ are probably due to the different cations. Ion association is probably also responsible for the low conductivities observed, *e.g.* for a (0·01/*n*)M solution of $[\{(cp)W(CO)_3Cu{\cdot}OH_2\}_n]$ in py $\kappa = 9{\cdot}0 \times 10^{-5}$ S cm^{-1} and is *ca.* $0{\cdot}1 \times 10^{-5}$ S cm^{-1} (but irreproducible due to extensive decomposition) in thf. The ionizations are at least largely reversible (*cf.* the preparations), but some decomposition occurs. The complexes $[\{(cp)M(CO)_3Ag\}_n]$ ionize similarly to $[Ag\{M(CO)_3(cp)\}_2]^-$. When M = W, a (0·01/*n*)M solution in py had $\kappa = 2{\cdot}4 \times 10^{-5}$ S cm^{-1}. However, other unidentified species are present (Table).

I.r. spectra in the ν(CO) region and conductivities show that $[\{Co(CO)_4Ag\}_n]$ and $[\{Co(CO)_4Cu(L)_y\}_n]$ ionize in donor solvents [for (0·01/*n*)M solutions of the former $\kappa = 0{\cdot}2 \times 10^{-5}$ S cm^{-1} in thf and $3{\cdot}7 \times 10^{-5}$ S cm^{-1} in py]. In thf both gave a single CO-containing species. By analogy with the behaviour of $[\{(cp)M(CO)_3M'\}_n]$ we suggest that these are $[M'\{Co(CO)_4\}_2]^-$. Furthermore, the observed i.r. spectra are similar to that of the isostructural neutral complex $[\{(OC)_4Co\}_2Hg]$.[16,17] These anions are present with neutral species in diethyl ether solutions. On the other hand, the i.r. spectrum of $[\{Co(CO)_4Cu(L)_y\}_n]$ in pyridine showed only a strong absorption band at *ca.* 1 890 cm^{-1} due to the well studied $[Co(CO)_4]^-$ ion.[18] With $[\{Co(CO)_4Ag\}_n]$, this second ionization is not complete and both $[Ag\{Co(CO)_4\}_2]^-$ and $[Co(CO)_4]^-$ ions are present in pyridine solution. The i.r. spectra of $[\{(Bu_3P)Co(CO)_3M'\}_n]$ and $[\{[(PhO)_3P]Fe(CO)_2(NO)Ag\}_n]$ are independent of solvent (Table).

The ionization of the Cr, Mo, and W derivatives in donor solvents is one aspect of their interaction with Lewis bases. Strong bases such as CN^- displace $[M(CO)_3(cp)]^-$ and phen acts similarly. The i.r. spectra of its insoluble 1 : 1 adducts show that the $[M(CO)_3(cp)]^-$ ions are the only CO-containing species present. Weaker bases such as $[M(CO)_3(cp)]^-$ act as ligands to Cu or Ag in $[\{(cp)M(CO)_3M'\}_n]$ without apparent rearrangement, thus allowing preparation of mixed anions, *e.g.* $[Me_4N][M'\{Mo(CO)_3(cp)\}\{W(CO)_3(cp)\}]$. On the other hand, Ph_3P converts $[\{(cp)M(CO)_3Cu(L)_x\}_n]$ only to $[(Ph_3P)_4Cu][Cu\{M(CO)_3(cp)\}_2]$.

The i.r. spectra of solid $[\{Co(CO)_4M'(phen)\}_n]$, $[\{Co(CO)_4Cu(bipy)\}_n]$, and $[\{[(PhO)_3P]Fe(CO)_2(NO)Ag(phen)\}_n]$ are complicated. The relatively low frequencies of the ν(CO) and ν(NO) absorption bands imply that metal-carbonyl anions are present. The i.r. spectra of $[\{(Bu_3P)Co(CO)_3M'(phen)\}_n]$ in thf show that only $[\{(Bu_3P)Co(CO)_3M'\}_n]$ is present when M′ = Ag but is absent when M′ = Cu. On addition of excess of phen, $[\{(Bu_3P)Co(CO)_3Ag\}_n]$ is replaced by a red complex

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* This applies equally to the solid state, *e.g.* the spectrum of a Nujol mull of $[\{(cp)W(CO)_3Ag\}_n]$ shows broad adsorption bands with irregular profiles at *ca.* 1 854s, 1 892w, and 1 939m cm^{-1} (*cf.* Table), but an ionic formulation, $[M']^+[M'\{M(CO)_3(cp)\}_2]$, cannot be discounted.

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and the relative concentrations of the two species present when $M' = Cu$ are changed. Solutions of $[\{(Bu_3P)Co(CO)_3Ag(dppe)\}_n]$ in CS_2 contain $[\{(Bu_3P)Co(CO)_3Ag\}_n]$ and another carbonyl complex. Only $[V(CO)_6]^-$ may be detected by i.r. spectroscopy in thf solutions of $[\{V(CO)_6Cu(phen)_2\}_n]$ or $[\{V(CO)_6Cu(bipy)\}_n]$. In chloroform, there were extra absorption bands at higher frequencies, similar to those due to the ν(CO) modes of $[V(CO)_6HgEt]$,[19] which may be due to species with covalent Cu–V bonds.

The inherently greater Lewis acidity of copper(I) over silver(I) is well known,[11] and is consistently manifested throughout this work. For example, one should compare the formulae of $[\{(cp)W(CO)_3Ag\}_n]$ and $[\{(cp)W(CO)_3Cu{\cdot}OH_2\}_n]$, where the H_2O ligand is almost certainly co-ordinated to copper, or the stabilities of $[\{(Bu_3P)Co(CO)_3Ag(phen)\}_n]$ and $[\{(Bu_3P)Co(CO)_3Cu(phen)\}_n]$ towards loss of phen. However, it is noticeable that replacement of CO in the metal-carbonyl anion by the weaker π-acceptor–stronger σ-donor ligand Bu_3P decreases the acidity of the Cu or Ag atom.

The conversion of $[Ag\{M(CO)_3(cp)\}_2]^-$ to $[\{(cp)M(CO)_3Ag\}_n]$ by $Et_2O{\cdot}BF_3$ is the reverse of the reaction of the neutral oligomers with some Lewis bases. The cleavage reactions of $[M'\{M(CO)_3(cp)\}_2]^-$ are neither unexpected nor unusual. They parallel those of neutral complexes such as $[\{(cp)(OC)_3M\}_2Hg]$, *e.g.* refs. 7, 20, and 21. Related complexes of gold(I) could not be prepared from solid gold(I) iodide. Also the series could not be extended to silver or copper derivatives of the metal-carbonyl anions $[Fe(CO)_2(cp)]^-$, $[Mn(CO)_5]^-$, or $[Mn(CO)_4(PEt_3)]^-$.

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