In summary, nine group 6 metal carbonyl complexes of 1-(diphenylphosphino)-3-(alkylphenylphosphino)propane have been prepared and examined by ^{31}P NMR spectroscopy. The data along with the previous data from the analogues $[Ph_2P(CH_2)_2PR^1R^2]M(CO)_4$ and $[Ph_2PCH_2PR^1R^2]M(CO)_4$ have been used to demonstrate that the overall phosphorus–phosphorus coupling constants in these compounds can be separated into two components: transmission via the σ bonds in the ligand backbone and via the σ bonds through the metal center.

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Registry No. $L_ICr(CO)_4$, 62264-02-2; $L_IMo(CO)_4$, 62263-98-3; $L_IW(CO)_4$, 62263-97-2; $L_{II}Cr(CO)_4$, 62263-96-1; $L_{II}Mo(CO)_4$, 62263-95-0; $L_{II}W(CO)_4$, 62263-94-9; $L_{III}Cr(CO)_4$, 62263-93-8; $L_{III}Mo(CO)_4$, 62263-92-7; $L_{III}W(CO)_4$, 62263-91-6; L_IS_2, 62263-63-2; $L_{II}S_2$, 62263-62-1; $L_{III}S_2$, 62263-61-0; L_I, 57137-57-2; L_{II}, 57137-58-3; L_{III}, 57137-65-2; L, 6737-42-4; $Cr(CO)_6$, 13007-92-6; $Mo(CO)_6$, 13939-06-5; $W(CO)_6$, 14040-11-0.

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Reactions of Metal Carbonyl Complexes. 10.[1] Selenocarbonyl Complexes of Chromium(0), Manganese(I), and Rhenium(I)[2]

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Carbon diselenide reacts in the presence of PPh_3 with $(\eta^5\text{-}C_5H_4R)M(CO)_2(THF)$ (M = Mn, R = H, Me; M = Re, R = H) or $(\eta^6\text{-}C_6H_5CO_2Me)Cr(CO)_2(THF)$ to give the new selenocarbonyl complexes, $(\eta^5\text{-}C_5H_4R)M(CO)_2(CSe)$ and $(\eta^6\text{-}C_6H_5CO_2Me)Cr(CO)_2(CSe)$, and PPh_3Se. The spectroscopic properties (IR and ^1H NMR) of these complexes indicate that CSe is a better net electron-withdrawing (σ-donor + π-acceptor) group than both CO and CS.

Unlike CO, the related CS and CSe diatomic molecules are extremely unstable even at very low temperatures. Carbon monosulfide polymerizes, often explosively, above −160 °C,[4] while CSe has thus far eluded isolation,[5] although some data have been reported for its electronic spectrum.[6] Over the past 10 years, there have been numerous examples of CS stabilization by coordination to transition metals and thiocarbonyl complexes have been synthesized for all of the group 6B, 7B, and 8 metals with the exception of technetium and palladium.[7,8] Our research in this field has been concerned chiefly with the synthesis of complexes such as $(\eta^5\text{-}C_5H_5)Mn(CO)_2(CS)$ by the reactions of labile intermediate complexes with CS_2/PPh_3 (eq 1).[1,9]

$$\begin{gathered}(\eta^5\text{-}C_5H_5)M(CO)_2L + CS_2 + PPh_3 \\ \rightarrow (\eta^5\text{-}C_5H_5)M(CO)_2(CS) + PPh_3S + L \qquad (1) \\ M = Mn, Re;\ L = C_8H_{14}, THF\end{gathered}$$

We report here the extension of reaction 1 to the formation of the first examples of transition metal selenocarbonyl complexes using CSe_2/PPh_3 as the in situ source of CSe. It is evident that many more selenocarbonyls will probably be prepared in the near future because, shortly following our initial communication on this work,[10] Clark et al. reported briefly on the synthesis of $RuX_2(CO)(CSe)(PPh_3)_2$ [X_2 = Cl_2, Br_2, I(OH)] and also described the x-ray structure of the dichloro derivative.[11]

Experimental Section

The manganese complexes $(\eta^5\text{-}C_5H_4R)Mn(CO)_3$ (R = H, Me) were generous gifts from the Ethyl Corp., New York, N.Y. The other starting materials were prepared by the literature methods indicated: $(\eta^5\text{-}C_5H_5)Re(CO)_3$,[12] $(\eta^6\text{-}C_6H_5CO_2Me)Cr(CO)_3$.[13] Triphenylphosphine (Aldrich Chemical Co.) was used without further purification. Carbon diselenide was purchased from Strem Chemicals Inc., Danvers, Mass. All solvents were distilled under nitrogen prior to use.

Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory Inc., Woodside, N.Y. Melting points were taken on a Gallenkamp apparatus and are uncorrected. Infrared spectra were recorded as described previously (accuracy ±1 cm^{-1}).[1] Mass spectra were obtained at 50–150 °C on an AEI-MS902 spectrometer operating at 70 eV. ^1H NMR spectra were measured at ~35 °C

Table I. IR Data for the New Selenocarbonyls and Related Complexes in CS_2 Solution (cm^{-1})$^{a-c}$

Complex	ν(CO)	ν(CX)	k_{CO}, mdyn Å^{-1}	k_{CX}, mdyn Å^{-1}
(η^5-C_5H_5)Mn(CO)$_3$	2022, 1926		15.49	
(η^5-C_5H_5)Mn(CO)$_2$(CS)	2000, 1949	1267	15.74	8.26
(η^5-C_5H_5)Mn(CO)$_2$(CSe)^d	2010, 1960	1107	15.92	7.53
(η^5-C_5H_4Me)Mn(CO)$_3$	2019, 1932		15.54	
(η^5-C_5H_4Me)Mn(CO)$_2$(CS)	2000, 1949	1265	15.74	8.22
(η^5-C_5H_4Me)Mn(CO)$_2$(CSe)	2003, 1953	1106	15.80	7.51
(η^5-C_6H_5)Re(CO)$_3$	2024, 1937		15.55	
(η^5-C_5H_5)Re(CO)$_2$(CS)	1998, 1931	1277	15.63	8.41
(η^5-C_5H_5)Re(CO)$_2$(CSe)	2005, 1946	1124	15.77	7.76
(η^6-$C_6H_5CO_2$Me)Cr(CO)$_3$	1984, 1916		15.20	
(η^6-$C_6H_5CO_2$Me)Cr(CO)$_2$(CS)	1980, 1940	1224	15.51	7.70
(η^6-$C_6H_5CO_2$Me)Cr(CO)$_2$(CSe)	1986, 1946	1063	15.61	6.94

^{a} All of the bands are strong. In order of decreasing energy, the assignments of the ν(CO) modes in the M(CO)$_3$ and M(CO)$_2$(CX) moieties are a_1 and e, and a′ and a″, respectively. All of the ν(CX) modes have a′ symmetry. ^{b} The force constants for "free" CS (trapped in a CS_2 matrix at −196 °C, 1259 cm^{-1})[30] and CSe (extrapolated value from the electronic spectrum, 1036 cm^{-1})[6] are 8.15 and 6.59 mdyn Å^{-1}, respectively. ^{c} All of the data for the tricarbonyls and thiocarbonyls are from ref 26. ^{d} In solid-state Raman spectrum (Kr^+ excitation): ν(CO) 1990 (s), 1959 (s); ν(CSe) 1084 (m) cm^{-1}.[23]

(instrument temperature) on a Varian T-60 spectrometer for saturated CS_2 solutions of the complexes containing ~10% TMS (accuracy ±0.1 ppm).

All operations were performed routinely under a nitrogen atmosphere. The photochemical reactions were carried out in Pyrex vessels fitted with water-cooled quartz fingers; these irradiation vessels are similar in design to that described by Ströhmeier.[14] The UV source [100-W Hanovia (No. 6315-30), high-pressure quartz mercury-vapor lamp emitting mainly at 366.0 nm (Ace Glass Inc., Vineland, N.J.)] was located inside the quartz fingers.

Preparation of (η^5-C_5H_5)Mn(CO)$_2$(CSe).[15] Dry THF (1700 mL) was distilled directly into a photochemical reactor containing (η^5-C_5H_5)Mn(CO)$_3$ (1.57 g, 7.7 mmol). After wrapping with aluminum foil, the vessel was placed in an ice–water bath and the solution was irradiated until the 2017-cm^{-1} IR band of the tricarbonyl had virtually disappeared (~2 h). Carbon diselenide (1.0 g, 5.9 mmol) and PPh_3 (2.01 g, 7.7 mmol) were dissolved in THF (10 mL) and the mixture was syringed through a rubber septum cap fitted on a side arm of the irradiation vessel into a bright red solution which contained chiefly (η^5-C_5H_5)Mn(CO)$_2$(THF).[16] The reaction vessel was removed from the ice–water bath and the reaction mixture was allowed to stand with warm water (45–55 °C) passing through the quartz finger until the IR spectrum showed no ν(CO) bands due to the THF complex (1925 (s) and 1850 (s) cm^{-1}) (~10 min). Following solvent removal on a rotary evaporator, the brown, oily gum remaining was taken up in a minimum of hexanes and passed through an alumina filter prepared in hexanes.[17] After the solvent was stripped from the CH_2Cl_2 filtrate, the yellow residue was placed in an aluminum foil wrapped sublimer and golden crystals of the selenocarbonyl derivative were sublimed at 25 °C (0.005 Torr) (yield 0.54 g, 34%; mp 64–65 °C). Anal. Calcd for $C_8H_5O_2MnSe$: C, 36.0; H, 1.89; Mn, 20.6; Se, 29.6. Found: C, 36.1; H, 2.03; Mn, 20.3; Se, 29.6. Molecular weight: calcd, 268; found, 268 (mass spectrum, ^{80}Se). ^1H NMR (CS_2 solution): 4.8 ppm (singlet, C_5H_5).

Preparation of (η^5-C_5H_4Me)Mn(CO)$_2$(CSe). The synthesis of this complex closely followed that described above. After reaction of (η^5-C_5H_4Me)Mn(CO)$_3$ (1.39 g, 6.4 mmol) with CSe_2 (1.09 g, 6.4 mmol) and PPh_3 (1.68 g, 6.4 mmol) in THF (1700 mL), product workup afforded the monoselenocarbonyl derivative as a golden oil (30–60 °C (0.001 Torr); yield 0.9 g, 50%). Further purification was achieved by TLC on silica gel plates (Analtech Inc.; 20 × 20 cm, 1 mm thick, precoated) with hexanes. However, the complex was never obtained completely analytically pure, although its spectroscopic properties leave no doubt as to its identity. Anal. Calcd for $C_9H_7O_2MnSe$: C, 38.5; H, 2.51; Mn, 19.5. Found: C, 40.3; H, 2.88; Mn, 17.1. Molecular weight: calcd, 282; found 282 (mass spectrum, ^{80}Se). ^1H NMR (CS_2 solution): 1.9 (singlet, CH_3), 4.6 ppm (singlet, C_5H_4).

Preparation of (η^5-C_5H_5)Re(CO)$_2$(CSe). A THF solution (1700 mL) of (η^5-C_5H_5)Re(CO)$_3$ (1.01 g, 3.0 mmol) was irradiated at 0 °C until the ν(CO) IR bands of the tricarbonyl at 2018 and 1922 cm^{-1} had almost vanished (~2 h). To the resulting yellow solution, CSe_2 (0.51 g, 3.0 mmol) and PPh_3 (0.78 g, 3.0 mmol) in THF (10 mL) were added and the mixture was left standing at ~50 °C for ~3 h. Following the workup procedure described above, a hexanes solution of the product was absorbed onto an alumina filter prepared in hexanes. The product was released from the filter by passage of CH_2Cl_2 after washing copiously with hexanes. The solvent was removed from the filtrate on a rotary evaporator and repeated recrystallization of the residue from CH_2Cl_2/*n*-pentane mixtures at −78 °C afforded pale yellow crystals of the selenocarbonyl product (yield 0.37 g, 31%; mp 97–100 °C). Anal. Calcd for $C_8H_5O_2ReSe$: C, 24.1; H, 1.27; Re, 46.7. Found: C, 24.3; H, 1.00; Re, 47.0. Molecular weight: calcd, 400; found, 400 (mass spectrum, ^{80}Se and ^{187}Re). ^1H NMR (CS_2 solution): 5.4 ppm (singlet, C_5H_5).

Preparation of (η^6-$C_6H_5CO_2$Me)Cr(CO)$_2$(CSe). According to the usual procedure described above, a solution of (η^6-$C_6H_5CO_2$Me)Cr(CO)$_3$ (0.25 g, 0.9 mmol) in THF (175 mL) was irradiated for 2 h. A solution of CSe_2 (0.41 g, 1.5 mmol) and PPh_3 (0.78 g, 3.0 mmol) dissolved in THF (10 mL) was then added to the reaction mixture. After the mixture stood in the dark for ~2 h, the solvent was stripped off under reduced pressure and the residue was extracted in a minimum of hexanes. Following absorption of the filtered hexanes solution onto an alumina filter and subsequent elution with CH_2Cl_2, the selenocarbonyl complex was obtained as an orange-red solid after solvent evaporation (yield 0.07 g, 21%; mp 185 °C). Molecular weight: calcd, 336; found, 336 (mass spectrum, ^{80}Se). ^1H NMR (CS_2 solution): 3.8 (singlet , CH_3), 5.4 (singlet, C_6H_5), 6.0 ppm (multiplet, C_6H_5).

Isolation of PPh_3Se. In a typical case, the discarded filtrates and solid residues from the synthesis of one of the selenocarbonyl derivatives were collected together and the solvents were removed on a rotary evaporator. The dark residue remaining was extracted with warm C_6H_6 and any insoluble material was filtered off. The filtrate was concentrated under reduced pressure until crystals started to appear. Addition of CH_3OH and cooling to −78 °C caused precipitation of impure PPh_3Se. A second recrystallization gave a white crystalline solid [mp 193 °C (lit.[18,19] mp 188 °C)]. Anal. Calcd for $C_{18}H_{15}PSe$: C, 63.3; H, 4.40; P, 9.09; Se, 23.2. Found: C, 63.4; H, 4.69; P, 8.81; Se, 23.3. Molecular weight: calcd, 342; found, 342 (mass spectrum, ^{80}Se).

Force Constant Calculations. The CO and CX (X = S, Se) force constants given in Table I for the M(CO)$_3$ (C_{3v} symmetry) and M(CO)$_2$(CX) (C_s symmetry) moieties were calculated using the appropriate approximate secular equations.[20] The values used for μ_{CS} and μ_{CSe} were 0.1145 and 0.095 93 g^{-1}, respectively. Coupling between the CO and CX vibrators was ignored in these calculations. Recent complete normal-coordinate calculations for M(CO)$_5$(CS) (M = Cr, W) have shown this to be a valid assumption.[21]

Results and Discussion

The new selenocarbonyl complexes are air stable and soluble in most common organic solvents. However, in solution, gradual decomposition takes place, particularly if the solutions are not shielded from light. The local symmetry of the M(CO)$_2$(CSe) moieties is C_s and two IR-active ν(CO) modes (a′ + a″) and one ν(CSe) mode (a′) are expected for each complex, as is observed (Table I). The ν(CSe) and ν(CO) modes are of comparable intensity and, if we bear in mind the

IR absorptions reported for the $RuX_2(CO)(CSe)(PPh_3)_2$ complexes,[11] the ν(CSe) region in metal selenocarbonyls is 1137–1063 cm^{-1}. Raman data have thus far only been obtained for solid $(\eta^5\text{-}C_5H_5)Mn(CO)_2(CSe)$ and, in striking contrast to the lack of Raman activity of the ν(CS) mode in $(\eta^5\text{-}C_5H_5)Mn(CO)_2(CS)$,[22] the ν(CSe) mode is readily attributable to a band at 1084 cm^{-1}.[23]

The mass spectra of the selenocarbonyls exhibit numerous fragment ions containing metal–CSe groups which are of much greater intensity than the corresponding metal–CO fragments. These results are at least tentatively indicative of the stronger metal–CSe bonding compared to metal–CO. A detailed analysis of the these mass spectra and those of closely related complexes will be reported elsewhere.[24]

Although x-ray studies are essential, it is most likely that the CSe groups in the complexes are attached to the metals through carbon and the metal–C–Se linkages are linear, as is the case for $RuCl_2(CO)(CSe)(PPh_3)_2$.[11] In other words, the bonding in metal–C–Se moieties is probably entirely analogous to that already well established for metal–C–O and metal–C–S groupings.

The mechanism for the formation of the selenocarbonyls is presumably similar to that established for the related thiocarbonyls,[9] e.g., for $(\eta^5\text{-}C_5H_5)Mn(CO)_2(CSe)$, the steps shown in (2). No IR evidence could be obtained for the

$$
\begin{aligned}
&(\eta^5\text{-}C_5H_5)Mn(CO)_2(THF)\\
&\quad \xrightarrow[+CSe_2]{-THF} (\eta^5\text{-}C_5H_5)Mn(CO)_2(\pi\text{-}CSe_2)\\
&\quad \xrightarrow{+PPh_3} (\eta^5\text{-}C_5H_5)Mn(CO)_2(CSe) + PPh_3Se
\end{aligned}
\tag{2}
$$

π-CSe_2 intermediate owing to the presence of strong THF absorptions at 1100–950 cm^{-1}. However, the existence of such a π-CSe_2 species has recently been reported for iridium and platinum.[25]

The synthesis of $(\eta^5\text{-}C_5H_4R)M(CO)_2(CSe)$ (M = Mn, R = H, Me; M = Re, R = H) and $(\eta^6\text{-}C_6H_5CO_2Me)Cr(CO)_2(CSe)$ allows for the first time a direct comparison of the spectroscopic properties of coordinated CO, CS, and CSe in various series of closely related complexes. For this purpose, the ν(CO) and ν(CS) modes in the analogous tricarbonyl and monothiocarbonyl complexes have been included in Table I, together with the associated approximate primary CO and CX force constants. The absolute accuracy of these force constants is at best ±0.2 mdyn $Å^{-1}$, particularly for k_{CX} where more extensive coupling between the CX and metal–CX vibrators is expected.[21] Despite this, the trends within all four series of complexes on descending the chalcogen group from oxygen to selenium are identical—there is an increase in k_{CO} and a concomitant decrease in k_{CX}. The ^1H NMR chemical shifts of the ring protons in the complexes also show variation with change in chalcogen. Although the shifts involved are extremely small, it is clear from Figure 1 that there is a distinct downfield chemical shift in the C_5H_5 protons in going from $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ to $(\eta^5\text{-}C_5H_5)Mn(CO)_2(CSe)$. Similar shifts are observed for the three other series.[26]

Both the increase in k_{CO} and the deshielding of the ring protons relative to the values for the tricarbonyl complexes upon replacing CO by CS and CSe are indicative of less electron density on the metal. Moreover, CSe is apparently a better net electron-withdrawing (σ-donor + π-acceptor) group than CO and CS.[27] The small downfield shifts of the ring protons can best be explained by an increased ring π-bond order resulting from a decrease in metal-to-ring d–π^* back-bonding. This in turn should lead to a weakening of the metal–ring bonding on descending the chalcogen group. Recent Raman data for the ν(Mn–ring) mode in the η^5-cyclopentadienylmanganese complexes support this assertion:[28] $(\eta^5\text{-}C_5H_5)Mn(CO)_3$, 355 cm^{-1};[29] $(\eta^5\text{-}C_5H_5)Mn(CO)_2(CS)$, 342 cm^{-1};[22] $(\eta^5\text{-}C_5H_5)Mn(CO)_2(CSe)$, 292 cm^{-1}.[23]

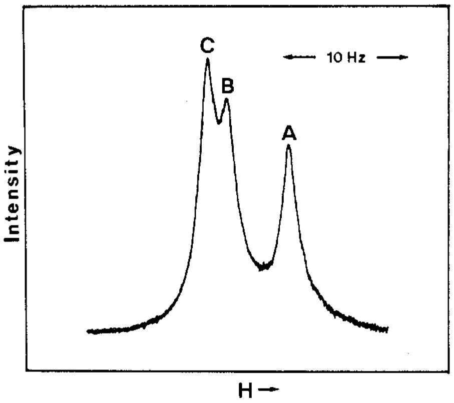

Figure 1. Expanded ^1H NMR spectrum in the region of 4.8 ppm of an approximately equimolar mixture in CS_2 solution of (A) $(\eta^5\text{-}C_5H_5)Mn(CO)_3$, (B) $(\eta^5\text{-}C_5H_5)Mn(CO)_2(CS)$, and (C) $(\eta^5\text{-}C_5H_5)Mn(CO)_2(CSe)$ illustrating the small downfield chemical shift of the C_5H_5 resonance on descending the chalcogen group.

Although it appears that k_{CS} and k_{CSe} increase upon complex formation relative to the values for the "free" ligands, this may be misleading because of the extent of coupling between the CX and metal–C(X) motions. In fact, normal-coordinate calculations on $M(CO)_5(CS)$ (M = Cr, W) show that there is a decrease in k_{CS} consistent with the synergistic bonding expected for M–CS bonding.[21]

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Registry No. $(\eta^5\text{-}C_5H_5)Mn(CO)_3$, 12079-65-1; $(\eta^5\text{-}C_5H_5)Mn(CO)_2(CSe)$, 55987-17-2; $(\eta^5\text{-}C_5H_4Me)Mn(CO)_3$, 12108-13-3; $(\eta^5\text{-}C_5H_4Me)Mn(CO)_2(CSe)$, 61421-10-1; $(\eta^5\text{-}C_5H_5)Re(CO)_3$, 12079-73-1; $(\eta^5\text{-}C_5H_5)Re(CO)_2(CSe)$, 61462-61-1; $(\eta^6\text{-}C_6H_5CO_2Me)Cr(CO)_3$, 12125-87-0; $(\eta^6\text{-}C_6H_5CO_2Me)Cr(CO)_2(CSe)$, 55923-60-9; $(\eta^5\text{-}C_5H_5)Mn(CO)_2(CS)$, 31741-76-1; PPh_3Se, 3878-44-2; CSe_2, 506-80-9.

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Group 1B Organometallic Chemistry. 18. Novel Routes to Stable Hexanuclear Copper–Silver, Silver–Gold, and Copper–Gold Cluster Compounds Starting from Polymeric 2-(Dimethylamino)phenylcopper and from Bis[(2-dimethylamino)phenyl]goldlithium Dimer[1]

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Mixed hexanuclear copper–silver, silver–gold, and copper–gold complexes of the type $R_4M_4M'_2X_2$ have been prepared via the reaction of 2-(dimethylamino)phenylcopper (RCu) with CuOTf or AgOTf (OTf = trifluoromethanesulfonato) as well as via the reaction of cuprous halide, of CuOTf, or of AgOTf with the novel bis[2-(dimethylamino)phenyl]goldlithium dimer $R_4Au_2Li_2$. IR and NMR spectroscopies reveal a structure for the $R_4M_4M'_2X_2$ compounds which is similar to the structure of $R_4Cu_6Br_2$ (x ray), i.e., a hexanuclear cluster structure with the (2-dimethylamino)phenyl ligands spanning triangular faces of the mixed $M_4M'_2$ core by 2e–3c carbon–metal and by 2e–2c metal–nitrogen bonds. The gold atoms in $R_4M_4Au_2X_2$ (M = Cu or Ag) occupy apical positions which is in line with the strong preference of gold(I) for a digonal coordination geometry. $R_4Cu_4Ag_2(OTf)_2$ is not stable and decomposes into R–R, $R_4Cu_6(OTf)_2$, and metallic silver at room temperature. Dynamic NMR spectroscopy reveals that the NMe_2 grouping is an excellent probe for the detection and elucidation of the dissymmetry in the cluster (R groups bridge unlike metal atoms; metal–N(Me_2) coordination renders the NMe_2 grouping a stable prochiral assembly). NMe resonances in $R_4Cu_4Au_2X_2$ remain anisochronous up to 90 °C, whereas those of $R_4Cu_6X_2$ coalesce at 40 °C. This has been explained in terms of increased $N-Cu_{eq}$ bond strength in the copper–gold derivative resulting from a contribution to the bonding of canonical structures such as $R_2Au^-[Cu_4X_2^{2+}]^-AuR_2$, in which 2e–3c RAuCu bonding has been replaced by 2e–2c RAu interactions. IR spectroscopy reveals that in spite of the weak electron-donor properties of the OTf anion the $R_4M_{6-n}M'_n(OTf)_2$ compounds (n = 0, 2) like the halide clusters $R_4M_{6-n}M'_nX_2$ (X = Br or I) are 84-electron species with each OTf anion contributing 4 electrons to the cluster by bridging two equatorial metal atoms. The similarity of the NMR patterns of $R_4Cu_4Au_2X_2$ (X = halide or OTf) derivatives in electron-pair-donating solvents such as pyridine can be explained both by metal core···anion dissociation resulting in 84-electron dications $R_4M_{6-n}M'_n(py)_4^{2+}$ or by cluster rearrangement affording $R_4M_{4-n}M'_n$.

Introduction

In previous reports we have shown that arylcopper compounds interact with metal halides. Electron-transfer,[1,3] transmetalation,[4,5] and complex formation reactions[2,3] have been identified for a number of different arylcopper derivatives. Both the substitution pattern of the aryl nucleus and the presence of heteroatoms in the substituents which coordinate with copper have proved to be decisive factors in determining the course of these reactions.

Recently we found[2] that interaction of polymeric 2-(dimethylamino)phenylcopper (I) with cuprous halides results in the formation of complexes $R_4Cu_6X_2$ which have discrete cluster structures consisting of $2-Me_2NC_6H_4$ groups bonded to a Cu_6 core by 2e–3c Cu–C and 2e–2c Cu–N bonds. The halide ligands bridge two equatorial Cu^I atoms by 4e–3c bonds (see Figure 1). In contrast, substitution of MeO for Me_2N results in a less specific aggregate formation,[6] whereas substitution of Me_2N by Me_2NCH_2 gives rise to the formation of polymeric species with RCu·CuX stoichiometry.[3,6]

The observation that the $2-Me_2NC_6H_4$ has the unique property of spanning octahedral faces of a Cu_6 core, which for example allows ligand substitution with retention of the R_4Cu_6 skeleton,[7,8] has provided further impetus to a study of the factors determining the stability of this type of 1B metal cluster compounds.

Substitution of copper atoms by silver atoms in $R_4Cu_6X_2$ results in the formation of species $R_4Cu_2Ag_4X_2$ and $R_4Cu_4Ag_2X_2$ having exactly the same overall stoichiometry.[9] NMR spectroscopy unambiguously showed that these mixed-metal species are not stable in solution and enter into interaggregate exchange reactions resulting in an equilibrium mixture of the various possible hexanuclear species $R_4Cu_{6-n}Ag_nX_2$ (n = 1–5).[2] These exchange phenomena can be rationalized on the basis of the different coordination symmetry of the apical and equatorial sites in hexanuclear $R_4M_6X_2$ clusters.[10a] Since both Cu^I and Ag^I can have digonal or trigonal coordination symmetries,[10b] these metals will not have a distinct preference for either the apical or equatorial sites in the $Cu_{6-n}Ag_n$ core. As a consequence the various $R_4Cu_{6-n}Ag_nX_2$ clusters will not differ greatly in stability. However, going down in the 1B metal series the preference for linear, twofold coordination increases. This is reflected in the fact that gold(I) complexes with trigonal coordination symmetry are exceptions.[10b,11] For this reason we anticipated increased stability for $R_4Cu_4Au_2X_2$ compounds because the gold(I) atoms can satisfy their preference for digonal coor-