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Preliminary Communication

THE LACK OF INTRAMOLECULAR CARBONYL LIGAND REARRANGEMENT IN THE STEREOSPECIFICALLY ^{13}CO LABELLED (DIAMINE)MOLYBDENUM TETRACARBONYL DERIVATIVES

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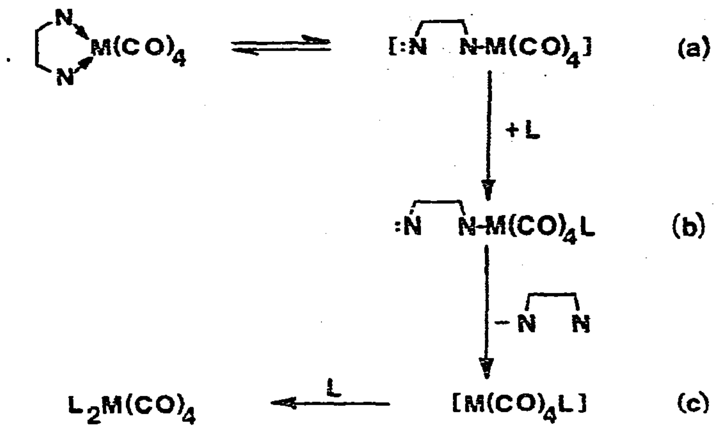
Summary

The preparation and spectral characterization of stereospecifically, axially labelled $Mo(CO)_3(^{13}CO)$(diamine) complexes (diamine = N,N,N',N'-tetramethylethylenediamine and N,N,N',N'-tetramethyl-1,3-diaminopropane) and the rigidity (or lack of fluxionality) of the carbonyl ligands during subsequent thermal reactions of these derivatives are reported.

In substitution processes involving the displacement of a bidentate ligand from a metal center in octahedral metal carbonyl complexes a rate determining step implicating chelate ring opening is widely accepted.[1-4] The incoming ligand thus competes with ring-closure for the five-coordinate intermediate. Indeed in one such process the intermediate containing one end of the bidentate ligand bound to the metal simultaneously with the incoming ligand occupying the sixth coordination site has been



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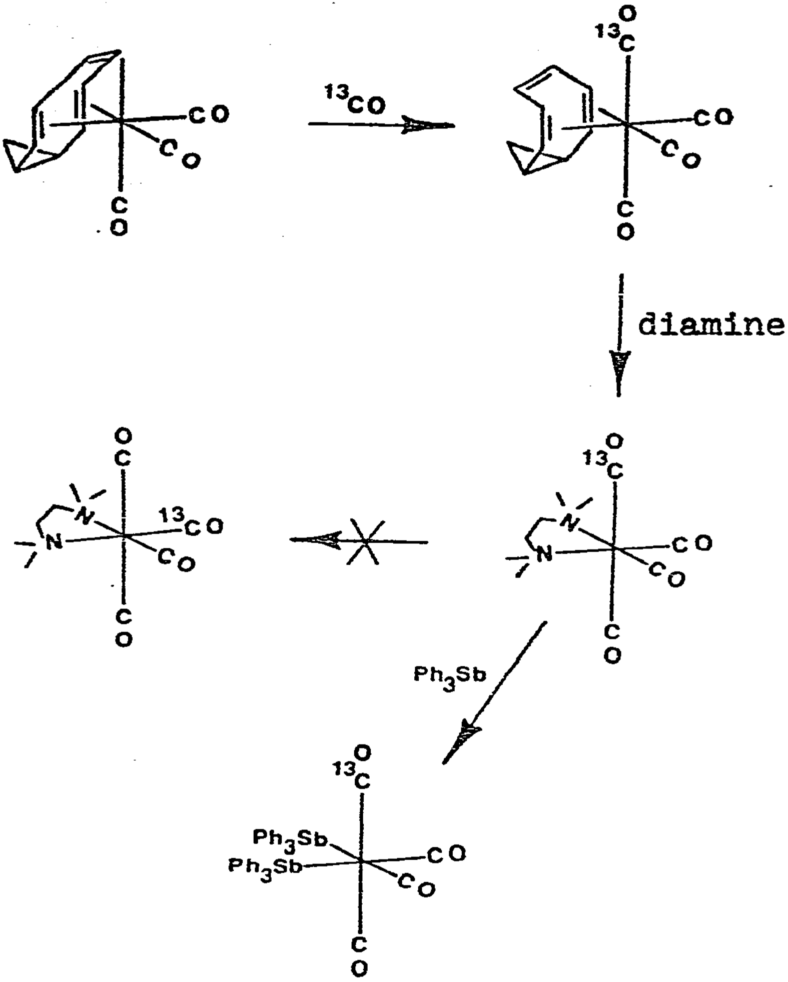
isolated and characterized.[5] Replacement of diamine ligands with phosphines are included in processes proposed to occur _via_ this mechanism (eq. 1).[6,7]

We have previously shown that the five-coordinate intermediate similar to (1a) which results from ring opening of the diene ligand in $W(CO)_4$(bicyclo[2.2.1]hepta-2,5-diene) is fluxional, i.e., the axial and equatorial CO sites intramolecularly exchange.[8] Likewise, [$Mo(CO)_5$], generated from the thermal dissociation of amine in $Mo(CO)_5$(amine), has been shown to be a fluxional species.[9] Therefore, if the reversible ring-opening mechanism described in eq. (1) is operative, an intramolecular rearrangement of CO groups might be anticipated in the substrate $Mo(CO)_4$(diamine) under conditions common to the substitution process. This communication reports on the preparation and spectral characterization (ν(CO) and ^{13}C nmr) of stereospecifically pure _fac_-$Mo(CO)_3(^{13}CO)$(diamine), diamine = N,N,N',N'-tetramethylethylenediamine and N,N,N',N'-tetramethyl-1,3-diaminopropane, and the nature of the intermediate $[:\overset{\frown}{N\ N}Mo(CO)_4]$ in its subsequent thermal substitution reactions.

Axially ^{13}CO labelled $Mo(CO)_4$(diamine) complexes were prepared from the very facile room temperature reaction of the

SCHEME



corresponding ^{13}CO labelled Mo(CO)$_4$(triene) species (triene = bicyclo[6.1.0]nona-2,4,6-triene) and the diamine ligands in hexane or chloroform (Scheme).[10]

The site of coordination of the ^{13}CO ligand in Mo(CO)$_4$-(diamine) was determined simultaneously by ν(CO) spectra (assigning all bands, both with respect to position and relative intensity pattern, with the aid of computations using a restricted CO force field) and by ^{13}C nmr measurements in the case of diamine = TMED. Table I contains the calculated and observed ν(CO) bands for the Mo(CO)$_4$(TMED) species along with the calculated CO force constants. The natural abundance ^{13}C nmr spectrum of $Mo(CO)_4(TMED)$ in chloroform gave two signals at 221.1 and 205.8 ppm as well as two signals due to the diamine ligand at 57.6 ppm (CH_2) and 55.8 ppm (CH_3); whereas, the ^{13}C-enriched sample at room temperature afforded only one strong signal at 205.8 ppm. The ^{13}C nmr results are therefore consistent with the axial ^{13}CO assignment based on $\nu(CO)$ spectral analysis. That is, all previous experience with two-electron ligands of poorer π-acidity than CO indicate that carbonyl ligands _trans_ to other carbonyl ligands yield a carbon resonance at lower frequency than carbonyl ligands _trans_ to the substituted ligand.[8,11]

As indicated in the Scheme the stereospecifically labelled $Mo(CO)_3(^{13}CO)$(diamine) species do not undergo intramolecular rearrangement thermally. For example, the samples were heated at 60° in hexane for up to an hour with no isomerization being observed.* This result is to be contrasted with the behavior of tetracarbonyl complexes of molybdenum with glyoxal bis(arylimines) where intramolecular cis/trans exchange of CO groups has been found to occur readily.[12] This process was proposed, however, to proceed _via_ a trigonal-prismatic transition state which involves no metal-nitrogen bond rupture. Further indications of the lack of axial and equatorial carbonyl ligand equilibration is obtained from the stereochemistry of the labelled carbon monoxide ligand in the product resulting from replacement of the diamine ligand with triphenylantimony. Table I contains the calculated and observed $\nu(CO)$ bands for the _cis_-$(Ph_3Sb)_2Mo(CO)_4$ species along with the calculated CO force constants. The natural abundance ^{13}C nmr spectrum of _cis_-$Mo(CO)_4[SbPh_3]_2$ in chloroform gave two signals in the carbonyl carbon region at 214.9 and

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*There is some decomposition in chloroform under these conditions which leads to a redistribution of carbon monoxide ligands intermolecularly.

Table I

Calculated and Observed CO Stretching Frequencies in (TMED)Mo(CO)$_4$ and *cis*-(Ph$_3$Sb)$_2$Mo(CO)$_4$ Species (cm^{-1})[a]

Molecule	Symmetry	Obsd[b]	Calcd
All ^{12}CO species	A_1	$\underline{2012.2}$ ($\underline{2022.7}$)	2012.6 (2023.2)
	A_1	$\underline{1888.0}$ ($\underline{1936.0}$)	1888.4 (1935.8)
	B_1	$\underline{1882.2}$ ($\underline{1920.4}$)	1883.9 (1920.1)
	B_2	$\underline{1856.2}$ ($\underline{1909.3}$)	1856.0 (1909.1)
Mono-^{13}CO,	A'	$\underline{2003.0}$ ($\underline{2010.6}$)	2002.8 (2011.2)
axially substituted	A'	$\underline{1887.0}$ ($\underline{1933.3}$)	1887.2 (1933.2)
	A'	$\underline{1854.3}$ ($\underline{1891.5}$)	1852.3 (1891.1)
	A''	1856.2 (1909.3)	1856.0 (1909.1)
Mono-^{13}CO,	A'	-- (d)	2004.6 (2018.4)
equatorially substituted	A'	-- (d)	1881.7 (1928.4)
	A'	1828.3[c] (d)	1828.5 (1878.3)
	A''	1882.2 (1920.4)[e]	1883.9 (1920.1)

[a] Frequencies were measured in hexane solution. The results for the triphenylantimony derivative are noted in parentheses. The $\nu(^{12}CO)$ values for (TMED)Mo(CO)$_4$ have previously been reported by R. Poilblanc and M. Bigorgne, J. Organomet. Chem., 5 (1966) 93.

[b] The seven frequencies (underlined) were used as input and were calculated with an average error of 0.7 cm^{-1} (0.3 cm^{-1}) or 0.039% (0.016%). Force constants calculated were: $k_1 = 14.59_0$ (15.12_9), $k_2 = 14.90_6$ (15.50_0), $k_c = 0.48_8$ (0.31_9), $k_c' = 0.68_1$ (0.41_4), and $k_t = 0.57_6$ (0.61_4), where k_1 and k_2 are equatorial and axial CO stretching force constants respectively, whereas, $k_c(CO_{ax}-CO_{eq})$, $k_c'(CO_{eq}-CO_{eq})$, and $k_t(CO_{ax}-CO_{ax})$ are the CO interaction force constants.

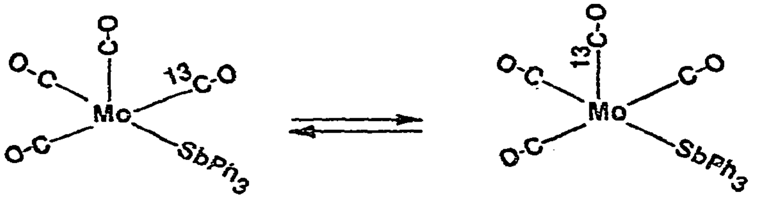
[c] This frequency was observed in the natural abundance ^{13}CO spectrum at high concentration.

[d] These frequencies were absent in the ^{13}CO labelled species.

[e] This frequency was not observed in the ^{13}CO enriched species. It is assigned based on the fact that it should be the same as the B_1 vibration in the all ^{12}CO species.

210.2 ppm; whereas, the ^{13}C-enriched sample gave only one strong signal at 210.2 ppm. Therefore, retention of the axial ^{13}CO label occurs during the substitution process. Since this reaction is thought to proceed <u>via</u> the process described in eq. 1, it therefore follows that not only is the intermediate [:$\overset{\frown}{N\ N}$Mo(CO)$_4$] non-fluxional but also must the intermediate [Ph$_3$SbMo(CO)$_4$] be non-fluxional (both these intermediates contain the substituted ligand in the equatorial plane).

These experimental results clearly substantiate the preference of L to occupy an equatorial position in [Mo(CO)$_4$L] species.[13] More importantly, these observations suggest the presence of a sizable barrier to thermal rearrangement of carbonyl ligands in the [Mo(CO)$_4$L] intermediates when L is quite different from carbon monoxide (eq. 2). On the other hand there are indications that this barrier is dependent on the nature of L and is less for tungsten derivatives.[8b]



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