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Preliminary communication

A THERMAL ROUTE TO STEREOSPECIFICALLY ^{13}CO LABELLED GROUP VIB METAL PENTACARBONYL AMINE DERIVATIVES

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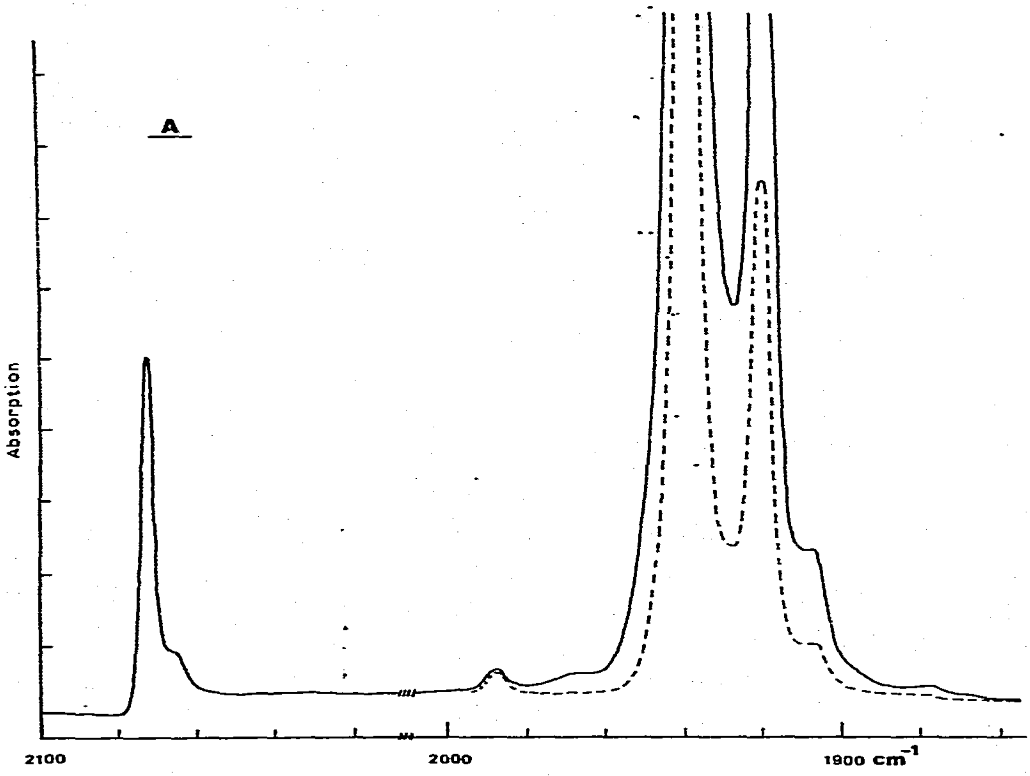
Summary

A method for the synthesis of stereospecifically, equatorially labelled *cis*-$M(CO)_4(^{13}CO)$(amine) derivatives where M = Cr, Mo, and W has been developed which involves ^{13}CO substitution into the vacant coordination site created by the facile dissociation of an amine ligand from *cis*-$M(CO)_4$(amine)$_2$ derivatives. The mechanistic implications of this extremely stereoselective reaction are discussed.

The synthetic capability to prepare stereospecifically or stereoselectively ^{13}CO or $C^{18}O$ labelled metal carbonyl derivatives has led to an understanding of the mechanistic details of thermal and photochemical ligand substitution reactions that otherwise would have been inaccessible [1—16]. In this communication we wish to report on a convenient synthesis of ^{13}CO labelled *cis*-$M(CO)_4(^{13}CO)$(amine) derivatives, where M = Cr, Mo, W and amine = piperidine; and M = Mo, amine = pyridine.

Reactions of *cis*-$M(CO)_4$(amine)$_2$ derivatives, prepared from $M(CO)_6$ and the corresponding amine in refluxing hydrocarbon solvent [17], and > 90% ^{13}C-enriched carbon monoxide were carried out slightly above room temperature (30—40°C) in dichloromethane (eq. 1) in a vessel which allowed for the introduction of CO through a frit by way of a gas inlet tube (see ref. 18 for a detailed drawing of the reactor). The reaction period was generally for 3—20 minutes. It was necessary to saturate the solvent with ^{13}CO prior to introducing the bis-amine complexes, in order to obtain ^{13}C-enriched species of high isotopic purity, since these bis-amine derivatives are thermally unstable in solution and quite rapidly decompose to the metal pentacarbonyl amine derivatives. The products were purified by hexane extraction of the solid which remained after vacuum removal of dichloromethane. Upon reducing the volume of hexane, bright yellow crystals of pure *cis*-$M(CO)_4(^{13}CO)$(amine) derivatives were isolated.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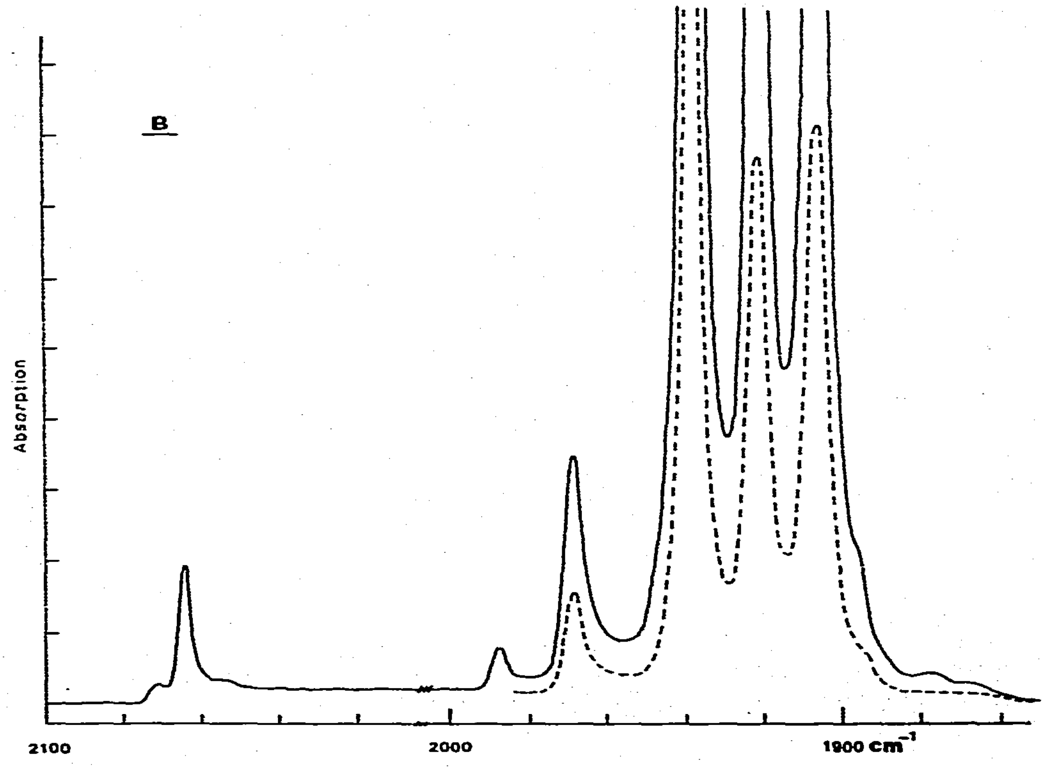
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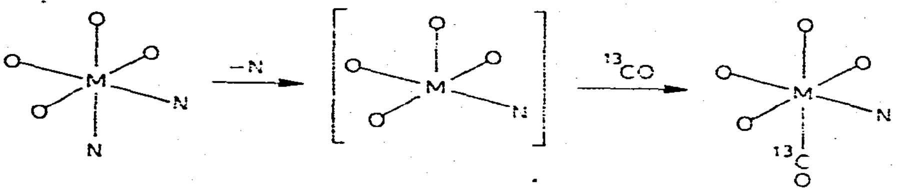

(1)

The site of coordination of the ^{13}CO ligand in these metal pentacarbonyl amine complexes was determined by their 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 [19]). Figure 1 depicts representative spectra of one of the isotopically labelled derivatives and its all ^{12}CO analog, *cis*-$Mo(CO)_4(^{13}CO)(NHC_5H_{10})$ and $Mo(CO)_5(NHC_5H_{10})$, in hydrocarbon solvents; whereas, Table 1 contains the calculated and observed ν(CO) bands along with the calculated CO force constants. As is readily seen in Fig. 1B, the band at 1878.6 cm^{-1} assigned to the *trans*-$Mo(CO)_4(^{13}CO)(C_5H_{10}NH)$ species is absent except at extremely high concentrations. Estimates of the stereoselectivity of ^{13}CO incorporation based on intensity ratio of the 1906.8 and 1878.6 cm^{-1} bands, as compared with the corresponding ratio in the natural abundance sample, indicate these reactions to be greater than 95% stereoselective or essentially stereospecific. We have previously reported on the preparation of stereoselectively, equatorially labelled $Mo(CO)_5(NHC_5H_{10})$ via photolysis of $Mo(CO)_5(NHC_5H_{10})$ in the presence of ^{13}CO [3]. More recently we have shown that in the primary photolytic process, the reaction of $M(CO)_5$(amine) derivatives with ^{13}CO is indeed stereospecific with equatorially enriched species being afforded [20]. However, photochemical preparative routes do not allow for the synthesis of singly labelled derivatives in their isotopically pure form.

TABLE 1

CALCULATED AND OBSERVED INFRARED FREQUENCIES IN THE ν(CO) REGION FOR THE ISOTOPIC SPECIES OF $Mo(CO)_5(NHC_5H_{10})$

Molecule	Frequencies (cm^{-1}) [a]				
All ^{12}CO	2073.5 (2073.5)	1990.0	1937.7 (1938.6)	1937.7 (1938.6)	1919.6 (1919.0)
Mono-^{13}CO (eq.)	2065.6 (2065.2)	1982.0	1937.7	1907.7 (1906.8)	1921.4 (1921.8)
Mono-^{13}CO (ax.)	2070.0	1990.0	1937.7	1937.7	1880.8 (1878.6) [b]

[a] Observed frequencies are listed in parentheses directly below the calculated values. The refined CO force constants calculated were: k_1 = 15.11, k_2 = 15.86, k_c = 0.361, k_c' = 0.285, and k_t = 0.699; see also ref. 19.
[b] This frequency was not observed in the ^{13}CO enriched sample except at extremely high concentrations.

As outlined in eq. 1, the stable form of the $[M(CO)_4(amine)]$ intermediate is assumed to be the C_s isomer where the amine ligand is in the equatorial plane of the square-pyramidal structure [21]. Reaction of this intermediate with an in-

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Fig. 1. (A) Natural abundance ^{13}CO spectra of $Mo(CO)_5(NHC_5H_{10})$ in hexane. (B) *cis*-$Mo(CO)_4(^{13}CO)(NHC_5H_{10})$ in hexane. The solid and dashed lines refer to two different concentrations.

coming labelled carbon monoxide thus affords the *cis*-$M(CO)_4(^{13}CO)$(amine) derivatives. Initial experiments in our laboratory on the reaction of *fac*-$Mo(CO)_3(C_5H_5N)_3$ with ^{13}CO indicate that each of the steps in the replacement of two of the pyridine ligands is stereospecific, eventually leading to *fac*-$Mo(CO)_3(^{13}CO)_2(C_5H_5N)$. This in turn requires that the carbonyl ligands in the intermediate in eq. 1, at least for M = Mo and amine = pyridine, be nonfluxional on the time scale for CO addition. Further evidence for the rigidity of the carbonyl ligands in $[Mo(CO)_4N]$ species has been presented in studies involving substitution reactions of stereospecifically labelled metal tetracarbonyl diamine derivatives [14].

Acknowledgements

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