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Preliminary communication

STEREOSPECIFIC INCORPORATION OF ^{13}CO INTO OLEFINIC SUBSTITUTED METAL CARBONYL COMPOUNDS

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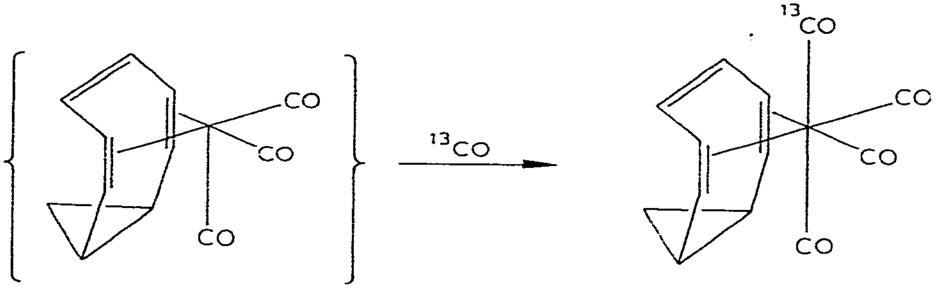
Summary

The triene complex, (bicyclo[6.1.0]nona-2,4,6-triene)molybdenum tricarbonyl, has been observed to react with ^{13}CO in solution to afford stereospecifically the axially labelled ^{13}CO tetracarbonyl derivative. Further reactions of this ^{13}CO derivative with triphenylphosphine or bis(1,2-diphenylphosphino)ethane resulted in formation of the *cis* disubstituted phosphine derivatives with retention of the ^{13}CO label.

An investigation of the reaction of (triene)Mo(CO)$_3$ with carbon monoxide to afford (triene)Mo(CO)$_4$ has been described [1]. This reaction presumably proceeds via metal—olefin bond cleavage of the unique olefinic group followed by addition of CO. In order to determine the coordination site of the incoming CO ligand we have carried out the olefin replacement reaction in the presence of ^{13}CO. The molybdenum tricarbonyl complex containing the bicyclic derivative of cyclooctatriene, (bicyclo[6.1.0]nona-2,4,6-triene)-molybdenum tricarbonyl, was reacted at room temperature with ^{13}CO in hydrocarbon solution. A 93% ^{13}CO enriched carbon monoxide atmosphere was continuously circulated through the tricarbonyl solution within a closed system by a variable speed Masterflex tubing pump. The extent of the reaction was followed by the disappearance of the orange-red color of the tricarbonyl species which gradually converted into the pale-yellow color of the tetracarbonyl complex (complete in ~ 20 min).

The infrared spectrum in the ν(CO) region indicated exclusive production of the axial ^{13}CO species (A in eq. 1).



(1)

(A)

The stereochemistry of the ^{13}CO species was based on assigning all the bands in the ν(CO) spectra, both with respect to position and relative intensity pattern, with the aid of computations using a restricted CO force field [2,3]*. Table 1 contains the calculated and observed ν(CO) bands for the (triene)-Mo(CO)$_4$ species along with the calculated CO force constants.

This result is consistent with other observations where substitution of a labile ligand with ^{13}CO has led to incorporation of carbon monoxide specifically at the site of the leaving group [4—6]. Further substitution reactions of the (triene)Mo(CO)$_3$ (^{13}CO) species with phosphines have yielded some very interesting results. Reaction of species A with excess triphenylphosphine in hydrocarbon or chloroform solution has afforded the *cis* disubstituted derivative where the axial ^{13}CO label has maintained its

TABLE 1

CALCULATED AND OBSERVED CO STRETCHING FREQUENCIES IN (triene)Mo(CO)$_4$ SPECIES[a]

Molecule	Symmetry	Obsd.[b]	Calcd.
All ^{12}CO species	A_1	*2044.0*	2043.7
	A_1	*1952.3*	1951.9
	B_1	*1969.0*	1969.4
	B_2	*1914.2*	1914.5
Mono-^{13}CO, axially substituted	A'	*2027.2*	2028.6
	A'	*1954.2*	1954.3
	A'	*1937.1*	1937.4
	A''	1914.2	1914.5
Mono-^{13}CO, equatorially substituted	A'	[c]	2042.4
	A'	[c]	1940.7
	A'	*1884.0*[d]	1883.8
	A''	[c]	1969.4

[a] Frequencies were measured in hexane solution. [b] The eight frequencies (italics) were used as input and were calculated with an average error of 0.4 cm^{-1} or 0.022%. Force constants calculated were: k_1 = 15.14(8), k_2 = 16.20(4), k_c = 0.19(8), $k_{c'}$ = 0.34(9), and k_t = 0.54(5), 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] These frequencies were absent in the ^{13}CO labelled species. [d] This frequency was observed in the natural abundance ^{13}CO spectrum at high concentration.

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* Although there is still some discussion concerning the use of force constants obtained by the method of restricted ν(CO) force fields, there is widespread agreement that ^{13}CO frequencies calculated by these procedures are correct [3].

integrity during the substitution process. That is, the axially labelled *cis*-$Mo(CO)_3(^{13}CO)(PPh_3)_2$ was formed exclusively. Similarly the substitution reaction with bis(1,2-diphenylphosphino)ethane (diphos) provided the axially labelled (diphos)$Mo(CO)_3(^{13}CO)$ species in near quantitative yield. The infrared spectra in the ν(CO) region of the ^{13}CO labelled phosphine products, coupled with frequency calculations and intensity patterns, unambiguously established the site of ^{13}CO in these derivatives.

The detailed mechanism for the substitution process involving replacement of the diene ligand in these type complexes by phosphines is currently under investigation in our laboratory. It is clear that there are distinct differences in the process reported here and replacement reactions involving loss of chelating diamines [6,7]. For example, in the substitution reaction of $Mo(CO)_4$(diamine) with PPh_3 both *cis*- and *trans*-$Mo(CO)_4(PPh_3)_2$ products are formed with the latter being predominant [7]. This product distribution in the case of the substitution reaction of $W(CO)_4$(diamine) with PPh_3 has been accounted for in terms of the fluxional behavior in the square pyramidal $[W(CO)_4PPh_3]$ intermediate [6]. The differences in these processes (olefin vs. amine substitution) may indeed arise from an interchange mechanism in the case of the olefin replacement where the leaving group plays a more important role.

Nevertheless, these observations clearly indicate that whatever the mechanistic details there is no scrambling of carbonyl groups in any of the transition states or intermediates involved in the substitution reaction of $Mo(CO)_4$(triene) with phosphines. In conclusion, this procedure provides an excellent method for the synthesis of stereospecifically labelled tetracarbonyl derivatives which are needed for ^{13}C NMR and mechanistic studies.

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