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Preliminary communication

STEREOSPECIFIC INTRODUCTION OF CARBON MONOXIDE INTO METAL CARBONYL CHELATE COMPLEXES

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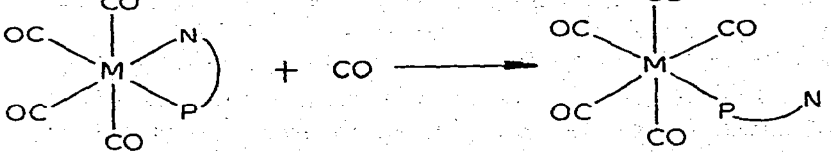
Summary

The chelate complex, $Mo(CO)_4[(C_6H_5)_2PCH_2CH_2CH_2N(CH_3)_2]$, reacts with ^{13}CO in solution with replacement of the N-donor end of the ligand giving *cis*-$Mo(CO)_4(^{13}CO)[(C_6H_5)_2PCH_2CH_2CH_2N(CH_3)_2]$ in which the ^{13}CO coordinates stereospecifically *cis* to the P atom; similarly the tridentate chelate complex, *cis*-$Mo(CO)_3[(C_6H_5)_2PCH_2CH_2N(C_2H_5)CH_2CH_2P(C_6H_5)_2]$, reacts with ^{13}CO to yield the N-displaced product in which the two P atoms remain coordinated *cis* to each other and the ^{13}CO coordinates *cis* to both P atoms. These remarkable stereospecific reactions with CO are discussed in terms of structures of possible reactive intermediates.

Kinetic studies of the reactions of a series of M(CO)$_4$(P—N) complexes with CO were recently carried out [1]:



(1)

where M = Cr, Mo, or W and P—N was a phosphorus—nitrogen bidentate donor ligand.

The results suggested a reaction mechanism involving slow dissociation of the N-donor end to give a five-coordinate intermediate which either underwent ring reclosure to regenerate the reactant or reacted with CO to give the product.

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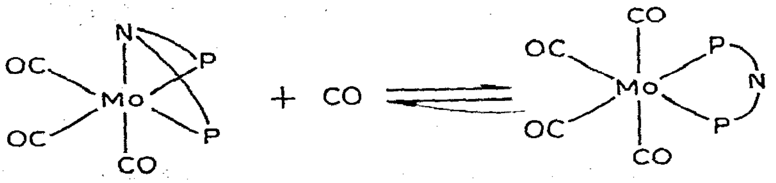
To determine the coordination position of the incoming CO in the product, the reaction was carried out using ^{13}CO. This was done by reacting to completion 0.55 g of $Mo(CO)_4[(C_6H_5)_2PCH_2CH_2CH_2N(CH_3)_2]$ with 1 atm of 90.7 mole % ^{13}CO in 50 ml $CHCl_3$ at 50.0° for 2.5 h. After evaporating the solution to dryness, the product was dissolved in CH_2Cl_2 for ^{13}C NMR analysis and in hexane for IR analysis. Infrared spectra of the hexane solutions at room temperature showed no changes over 48 h, indicating that isomerization did not occur during this period. The ^{13}C spectrum [2] showed only a sharp doublet ($^2J(^{31}P^{13}C)$ 8.8 ± 0.5 Hz) at δ 199.4 ppm downfield from tetramethylsilane. The small magnitude of the coupling constant [3, 4], indicates that the ^{13}CO is *cis* to the phosphorus atom in the $Mo(CO)_4(^{13}CO)[(C_6H_5)_2PCH_2CH_2CH_2N(CH_3)_2]$ product.

The infrared spectrum of the hexane solution showed $\nu(C{\equiv}O)$ absorptions at 2064m, 1980w, 1952vs(sh), 1946vs, 1929m, and 1916s cm^{-1}. Using frequencies (2072m, 1984w, 1951vs(sh), and 1944vs cm^{-1}) for the all-^{12}CO complex, and assuming the ^{13}CO to be *cis* to the P atom, frequencies for *cis*-$Mo(CO)_4(^{13}CO)[(C_6H_5)_2PCH_2CH_2CH_2N(CH_3)_2]$ were calculated as previously described [5] to be within 2 cm^{-1} of those observed. An apparently spurious peak in the spectrum at 1929m has not been accounted for. There was no evidence for *trans* ^{13}CO substitution or for more than one ^{13}CO substitution into the molecule. Thus both the ^{13}C NMR and infrared results indicate that the ^{13}CO stereospecifically substitutes *cis* to the P atom. It should be noted that this result contrasts with the lack of stereospecific replacement of norbornadiene in $Mo(CO)_4(C_7H_8)$ by ^{13}CO. In that case, both *cis*- and *trans*-$Mo(CO)_4(^{13}CO)_2$ were formed [6].

A tridentate chelate complex which undergoes chelate ring-opening with CO was also studied [7]:



(2)

where P—N—P = $(C_6H_5)_2PCH_2CH_2N(C_2H_5)CH_2CH_2P(C_6H_5)_2$, PNP.

The infrared spectrum of the product (2019w, 1926m, 1906vs, and 1899s cm^{-1} in hexane) establishes its *cis* structure as shown in equation (2).

To determine the coordination site of the incoming CO, 0.53 g of $Mo(CO)_3(PNP)$ [8] was treated at 60° in 40 ml $CHCl_3$ with 1 atm of 90.7 mol % ^{13}CO for 12 h. The solid remaining after vacuum evaporation was dissolved in CH_2Cl_2 for the NMR studies and in hexane for the infrared studies. The ^{13}C NMR spectrum showed only a strong triplet ($^2J(^{31}P^{13}C)$ 9.5 ± 0.5 Hz) at 17.4 ± 0.1 ppm downfield from internal CS_2, indicating ^{13}CO coupling to two equivalent *cis* P atoms. This would be expected for ^{13}CO coordination at the position vacated by the N atom. When converted to a tetramethylsilane (TMS) reference scale, the chemical shift is approximately 210 ppm downfield from TMS. This value and the associated $^2J(^{31}P^{13}C)$ coupling constant are very similar to the analogous parameters reported [4] for the ^{13}CO group *cis* to the P atoms in $Mo(CO)_4[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]$.

The infrared spectrum showed bands at 2008m, 1920m, 1899s, 1883m, and 1872m cm^{-1}. The positions of the four highest frequency bands are in good agreement with values calculated for $Mo(CO)_3(^{13}CO)(PNP)$ in which the ^{13}CO is *cis* to both P atoms. The absence of an absorption at ~2018 cm^{-1}, expected for the isomer with ^{13}CO *trans* to a P atom, rules out the presence of that isomer. Thus both the ^{13}C NMR and infrared results support ^{13}CO substitution only in a position *cis* to both P atoms of the product.

When a $CHCl_3$ solution of the *cis*-$Mo(CO)_3(^{13}CO)(PNP)$ was warmed at 60° for 2 h under an N_2 atmosphere, the compound released CO to return to the starting tricarbonyl compound (reverse of eqn. 2). The infrared spectrum of this product was extremely complex. However, it was possible to assign bands to the two possible isomers of $Mo(CO)_2(^{13}CO)(PNP)$ in which the ^{13}CO group was either *cis* or *trans* to the N donor atom. This lack of stereospecificity in the reverse of reaction (2) suggests that both *cis* and *trans* CO groups in $Mo(CO)_3$-$(^{13}CO)(PNP)$ may be dissociating in this reaction or that CO scrambling is occurring in the 5-coordinate intermediate.

In the forward reactions of both eqns. (1) and (2), however, the incoming ^{13}CO is stereospecific in coordinating *cis* to the P atoms, which is also the site vacated by the N-donor group. The lack of random ^{13}CO substitution suggests that the five-coordinate intermediate with which the CO reacts either has a square pyramidal structure resulting directly from nitrogen dissociation or a trigonal bipyramidal structure in which ^{13}CO attacks specifically at a position *cis* to the P atoms [9].

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