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Preliminary communication

INSERTION OF CARBON DIOXIDE INTO MANGANAPHOSPHACYCLOALKANES

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Summary

Carbon dioxide inserts into the metal—carbon bond of 2,2,2,2-tetracarbonyl-1,1-diphenyl-1-phospha-2-manganacyclobutane to yield the manganacarbonyl complex $(OC)_4\overline{MnPPh_2CH_2CH_2COO}$, which is stabilized by a P/O-chelate ligand.

The insertion of carbon dioxide into transition metal—carbon bonds is assumed to be the initial key step of catalytic reactions involving CO_2 [1]. For that reason the study of stoichiometric reactions of carbon dioxide may supply important information about the utilization of CO_2 as a future raw material in chemical syntheses.

Insertions of CO_2 into metal—aryl and metal—alkyl bonds to form carboxylate complexes are well known reactions. The insertion of carbon dioxide into metallacycles has been less well studied, although such species are known to function as highly reactive intermediates in numerous transition metal catalyzed reactions such as oligomerization [2], isomerization [3] or metathesis [4]. An interesting case of insertion of carbon dioxide into a substituted nickelacyclopentane, has been noted in the catalytic oligomerization of allene, which involves a pentacoordinated allylnickel carboxylate complex [5]. Compounds in which a metal atom and a CO_2 molecule are combined in a metallacyclopentane are also known for titanium [6] and nickel [7]; but these complexes were formed by C—C coupling reactions and not by insertion of CO_2 into metallacycles.

We describe below the results of studies of the insertion of carbon dioxide into manganaphosphacycloalkanes. Insertion of CO_2 into the manganese—carbon bond is known to occur even at mild conditions; e.g. the complex $Ph_2Mn \cdot PCy_3$ reacts with carbon dioxide at room temperature [8] and insertion

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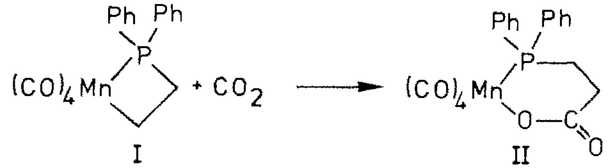
of CO_2 into $(PhCH_2)_2Mn$ occurs even at −5°C [9]. Insertion of CO_2 into the manganese—methyl bond has also been noted, but the carboxylate complex was not isolated [10].

Complex I, 2,2,2,2-tetracarbonyl-1,1-diphenyl-1-phospha-2-manganacyclobutane [11], was treated with carbon dioxide to yield a bright yellow solid. The best reaction conditions proved to involve a temperature of 50°C, a reaction time of 48 h, a fourhundred fold molar excess (related to the manganese complex) of carbon dioxide, and a non-polar solvent such as n-hexane from which the product precipitated. All the spectroscopic data are in agreement with the formulation II for the new insertion product.



The infrared spectrum of complex II, measured in KBr, shows a broad asymmetric signal at 1591 cm^{-1} and a symmetric signal at 1409 cm^{-1}, values close to those for the manganacarboxylates $Mn(OOCCH_2Ph)_2$ (ν_{as} 1570 cm^{-1}, ν_s 1415 cm^{-1}) and $Mn(OOCPh)_2PCy_3$ (ν_{as} 1550 cm^{-1}, ν_2 1400 cm^{-1}). Formation of a carbonate complex (which should have characteristic IR bands in the ranges of 1360—1380 cm^{-1} and 1525—1535 cm^{-1}) can be excluded. Useful information is also given by the shifts of the absorptions of the terminal carbonyl ligands. Table 1 compares the values for the starting complex I, the CO_2 insertion product II, and the known CO and SO_2 insertion products $(CO)_4\overline{MnPPh_2CH_2CH_2C}O$ (III) and $(CO)_4\overline{MnPPh_2CH_2CH_2S}O_2$ (IV) [11]. The shift to higher wave numbers, indicating a lowering of the Mn—CO back donation, falls in the order I < III < II < IV.

TABLE 1

COMPARISON OF THE IR SPECTRA OF COMPLEX I AND ITS INSERTION PRODUCTS (in cm^{-1})

Complex		$\nu(C{\equiv}O)$			
$(OC)_4\overline{MnPPh_2CH_2C}H_2$	(I)	2056	1987	1963	1939[a]
$(OC)_4\overline{MnPPh_2CH_2CH_2C}O$	(III)	2066	2003	1974	1965[b]
$(OC)_4\overline{MnPPh_2CH_2CH_2COO}$	(II)	2095	2021	2008	1953[a]
$(OC)_4\overline{MnPPh_2CH_2CH_2S}O_2$	(IV)	2098	2033	2018	1993[c]

[a] KBr. [b] CCl_4. [c] $CHCl_3$.

Infrared spectroscopy seems to be the best method of checking the purity of the manganese carboxylate complex II; the region of the terminal carbonyl bands being especially informative. The IR spectrum would show the presence of impurity responsible to complex III, which can be formed by a parallel intramolecular insertion of a carbon monoxide ligand into the Mn—C bond, since a sharp signal for C=O frequency at 1635 cm^{-1} (in KBr) should appear.

The ^1H NMR spectrum of complex II shows the aromatic protons and a broad multiplet of the four aliphatic protons in the range of 2.25 to 2.85 ppm. The signals for the two aliphatic protons in complex II, which are in α positions to the manganese are shifted by about 1.5 ppm to lower field compared with those in complex I.

The ^{13}C NMR spectrum of II shows a multiplet for the carbonyl carbons at 218 ppm and a singlet for the carboxylate carbon at 223 ppm. The ^{31}P NMR spectrum shows a singlet at 82.2 ppm (relative to H_3PO_4 as external standard), in the same range as the corresponding signal from the CO and SO_2 insertion products III and IV [11].

The mass spectrum of complex II (at 70 eV) contains peaks at m/e = 380 [$M - CO_2$], 352 [$M - CO_2 - CO$], 324 [$M - CO_2 - 2CO$], 296 [$M - CO_2 - 3CO$] and 268 [$M - CO_2 - 4CO$]. The base peak is that for the [$MnPPh_2$] fragment at m/e = 240.

Although the insertion of carbon dioxide occurs in satisfactory yields (up to 40%) in the case of the manganacyclobutane derivative I, no insertion was observed with the related manganacyclopentane derivative $(OC)_4\overline{MnPPh_2(C}H_2)_3$. Obviously the strain energy of the starting complex has a decisive effect on the insertion of carbon dioxide into metallacycles.

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