

Preliminary communication

REACTIONS OF $[\text{Mo}(\text{N}_2)_2(\text{dppe})_2]$ WITH ORGANIC ISOCYANATES

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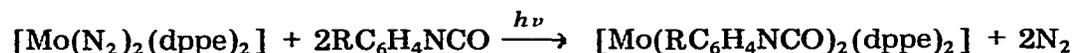
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Summary

The reactions of $[\text{Mo}(\text{N}_2)_2(\text{dppe})_2]$, ($\text{dppe} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$) with $\text{RC}_6\text{H}_4\text{NCO}$ ($\text{R} = \text{H}, p\text{-CH}_3, p\text{-Cl}$) in benzene under irradiation produces $[\text{Mo}(\text{RC}_6\text{H}_4\text{NCO})_2(\text{dppe})_2]$ in good yields. Comparison of the infrared data for these complexes, with those previously reported for metal complexes of CO_2 -like molecules suggest a $\eta^2\text{-C,O}$ coordination to the metal.

The dinitrogen complex *trans*- $[\text{Mo}(\text{N}_2)_2(\text{dppe})_2]$ (I) undergoes a variety of substitution reactions in which dinitrogen is partly or totally lost [1]. Ligands such as CO [2], RNC [3], RCN [4], $\text{P}(\text{OR})_3$ [5] are able to give σ -coordination at the electron-rich $\text{Mo}(\text{dppe})_2$ site, whereas ethylene and tetracyanoethylene (tcne) give η^2 -coordination, in $[\text{Mo}(\text{C}_2\text{H}_4)(\text{dppe})_2]$ and $[\text{Mo}(\text{tcne})_2(\text{dppe})_2]$, respectively [6]. Carbon dioxide reacts with *cis*- $[\text{Mo}(\text{N}_2)_2(\text{PMe}_2\text{Ph})_4]$, but not with I, to form a complex formulated as $[\text{Mo}(\text{CO}_2)_2(\text{PMe}_2\text{Ph})_4]$, (IR: 1760 cm^{-1}) [7], in which CO_2 is probably η^2 -bonded to the metal center.

We now report that aromatic isocyanates, which are CO_2 -like molecules, react with I, under irradiation, to give well defined substitution products of formula $[\text{Mo}(\text{RC}_6\text{H}_4\text{NCO})_2(\text{dppe})_2]$, ($\text{R} = \text{H}, p\text{-CH}_3, p\text{-Cl}$), according to the equation:



Aliphatic isocyanates, such as the methyl and *t*-butyl compounds give, after prolonged irradiation, only uncharacterized decomposition powders, whereas preliminary investigation have shown that PhNCS reacts readily with I without irradiation to give an S-containing molybdenum complex and free PhNC^* .

* $[\text{W}(\text{N}_2)_2(\text{dppe})_2]$ does not react with PhNCS under the same conditions. In contrast, it reacts with $p\text{-CH}_3\text{C}_6\text{H}_4\text{NCO}$ to produce a brown complex formulated as $[\text{W}(\text{N}_2)(\text{C}_7\text{H}_7\text{NCO})(\text{dppe})_2]$, (IR: 2000s, 1935vs, 1550s), but the low yield and the incomplete reproducibility of the results mean that further investigation is needed.

TABLE 1

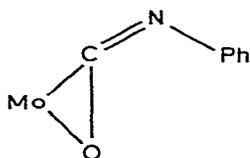
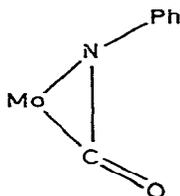
CHARACTERIZATION DATA FOR THE COMPLEXES $[\text{Mo}(\text{RC}_6\text{H}_4\text{NCO})_2(\text{dppe})_2]$

R ^a	IR bands (cm ⁻¹)			Color	M.P. (°C)
	$\nu(\text{CO})$	$\nu(\text{CN})$	other		
H	1620vs	1570vs	1485s, 1431s, 1226ms, 1092m	yellow	110(dec.)
<i>p</i> -CH ₃	1620vs	1588vs	1495vs, 1431s, 1223m, 1091m	yellow	110(dec.)
<i>p</i> -Cl	1620vs	1568vs	1480s, 1431ms, 1235m, 1091m	yellow	130(dec.)

^a All these complexes gave satisfactory elemental (C,H,N) analyses.

Characterization data for the isocyanate complexes are summarized in Table 1.

The major feature in the IR spectra of these compounds is the absence of any bands near 2200 cm⁻¹ attributable to the antisymmetric vibration of the heterocumulenes, and the presence of two very strong bands near 1600 cm⁻¹. The first band, assignable to $\nu(\text{CO})$, (1620 cm⁻¹), is completely independent of the nature of the *para*-substituent, whereas the second band (near 1570 cm⁻¹) shows a slight dependence. The values are consistent with η^2 -coordination of the isocyanates at the metal, but there remains the question of whether the η^2 -linkage involves the CO or the CN bond:

 $\eta^2 - \text{C}, \text{O}$  $\eta^2 - \text{C}, \text{N}$

There are only a few reports in the literature dealing with η^2 -bonded aromatic isocyanates, but their reactions with transition metal complexes have recently been reviewed [8]. Examples of products are $[\text{Ni}(\text{PPh}_3)_2(\text{PhNCO})]$, ($\nu(\text{CO})$, 1763 cm⁻¹; η^2 -C,N suggested), [9] and $[\text{RhCl}(\text{PCy}_3)_2(\text{PhNCO})]$, ($\nu(\text{CO})$, 1842 cm⁻¹; η^2 -C,N suggested) [10]; however, no crystal structure determination have appeared to confirm the proposed mode of bonding.

On the other hand, the binding modes of diphenylketene, Ph_2CCO , in its metal complexes have been clarified by X-ray structure determinations. For example it exhibits a η^2 -C,O coordination in $[\text{Cp}_2\text{V}(\text{Ph}_2\text{CCO})]$, ($\nu(\text{CO})$, 1620 cm⁻¹) [11], and a η^2 -C,C linkage in $[\text{CpMn}(\text{CO})_2(\text{Ph}_2\text{CCO})]$, ($\nu(\text{CO})$, 1787 cm⁻¹) [12]. The same low value for $\nu(\text{CO})$ found in $[\text{Cp}_2\text{V}(\text{Ph}_2\text{CCO})]$ and in $[\text{Mo}(\text{RC}_6\text{H}_4\text{NCO})_2(\text{dppe})_2]$ strongly suggests a η^2 -C,O coordination for the latter also, unlike the reported Ni and Rh complexes, in which PhNCO could be η^2 -C,N bonded.

An X-ray structural analysis, undertaken on the phenyl derivative $[\text{Mo}(\text{PhNCO})_2(\text{dppe})_2]$ with the best crystals we were able to obtain, allowed us to locate only the Mo atom and four electron density peaks attributable to P atoms. They were arranged in a nearly square planar fashion around the metal, at dis-

tances ranging from 2.52 to 2.55 Å. Any attempt to locate the remaining non-hydrogen atoms, including those occupying the apical positions in the Mo environment, failed, owing to the paucity of data (only 20% of observed reflections with $I \geq \sigma(I)$).

Experimental

All reactions were carried out under dinitrogen, using standard inert atmosphere techniques. Irradiation of solutions, in Pyrex vessels, were carried out with an Helios-Ital quartz high pressure 125W mercury lamp.

Preparation of $[\text{Mo}(\text{PhNCO})_2(\text{dppe})_2]$. *Procedure A*: phenyl isocyanate (2 mmol) was added to an orange benzene solution (20 ml) of I (0.1 mmol) (prepared as in ref. 13). The mixture was irradiated for 6 h at room temperature during which the color changed to yellowish brown. Addition of hexane and cooling gave a yellow microcrystalline product, which was filtered off, washed, and dried in vacuo (70%); (see Table 1). *Procedure B*: phenyl isocyanate (0.45 mmol) was added to a toluene solution (20 ml) of I (0.15 mmol) and the mixture was stirred at 0°C for 36 h. Hexane was added (15 ml) and the solution was kept at 4°C for two days. The resulting yellow prismatic crystals were filtered off, washed, and dried in vacuo. Analytical and ^1H NMR data support the formula $[\text{Mo}(\text{PhNCO})_2(\text{dppe})_2] \cdot \text{PhMe}$. Crystal data: $\text{C}_{73}\text{H}_{66}\text{MoN}_2\text{O}_2\text{P}_4$, monoclinic, space group $P2_1/c$, a 18.53, b 27.23, c 12.92 Å, β 90.2°, $Z = 4$. The other complexes were prepared, in similar yields, by procedure A.

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