

Preliminary communication

REACTIONS OF $M_2Cl_4(PR_3)_4$ ($M = Mo$ AND W) WITH CARBON MONOXIDE

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Summary

The reactions of $M_2Cl_4(PR_3)_4$ derivatives ($M = Mo, W$ and $PR_3 = PEt_3, PBu_3^n$) with CO at atmospheric pressure in toluene at 70°C to afford $M(CO)_3(PR_3)_2Cl_2$ and *trans*- $M(CO)_4(PR_3)_2$ are reported.

Although simple adduct formation and ligand substitution processes involving quadruply bonded metal–metal dimers with donor ligands such as phosphines have been described [1–4], little is known regarding reactivity patterns in these species with good π -acceptor ligands. The reactions of $Mo_2(O_2CCH_3)_4$ and $K_4Mo_2Cl_8$ with alkyl isocyanides were found to cleave the Mo–Mo quadruple bond to provide $[Mo(CNR)_7]^{2+}$ ions [5], and $Mo_2Me_4(PR_3)_4$ compounds have been shown to react with CO to give acetone and mononuclear, zero-valent molybdenum species $Mo(CO)_{6-x}(PR_3)_x$ where $x = 0–3$ [4]. We have begun a systematic investigation of the reactivity of quadruply bonded metal–metal derivatives with carbon monoxide, and we report here some of our initial observations [6].

A Schlenk flask containing a toluene solution of $Mo_2Cl_4(PEt_3)_4$ was charged with an atmosphere of carbon monoxide. Upon heating to 70°C the reaction solution gradually (over ca. 1 h) changed in appearance from the deep blue color of the starting reagent to a red-orange color. The reaction was monitored in the $\nu(CO)$ region by means of infrared spectroscopy and it showed a constant band profile, both with respect to number and relative intensities (see Fig. 1), over the duration of the reaction. The three bands at 2019, 1947, and 1906 cm^{-1} can be shown to belong to $Mo(CO)_3(PEt_3)_2Cl_2$, while the peak at 1881 cm^{-1} is attributable to the *trans*- $Mo(CO)_4(PEt_3)_2$ derivative. These $\nu(CO)$ band assignments were confirmed by spectral comparisons with authentic samples obtained from independent syntheses employing established techniques [7,8]. The stereochemistry of the seven-coordinate monomer,

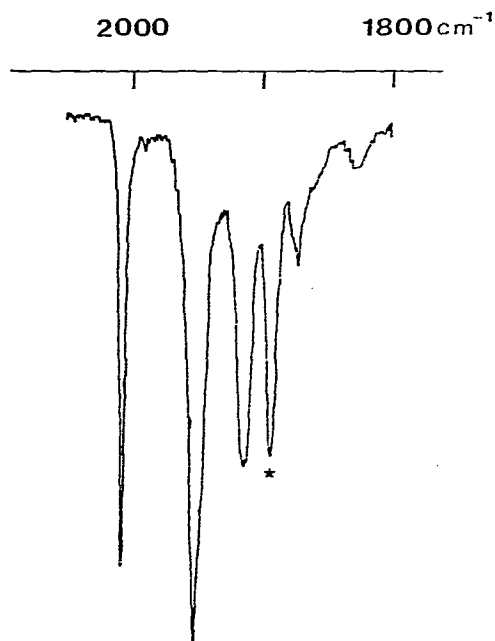


Fig. 1. Infrared spectrum in $\nu(\text{CO})$ region in toluene of CO-containing products from the reaction of $\text{Mo}_2\text{Cl}_4(\text{PEt}_3)_4$ with CO at 70°C . Peak marked with asterisk is due to $\text{trans-Mo}(\text{CO})_4(\text{PEt}_3)_2$.

$\text{Mo}(\text{CO})_3(\text{PEt}_3)_2\text{Cl}_2$, obtained from the reaction of $\text{Mo}(\text{CO})_4\text{Cl}_2$ and PEt_3 [9], has been determined by a single crystal X-ray diffraction study [9]. The complex exists as a capped octahedron with a CO ligand occupying the capping position, two CO groups and one phosphine ligand in the capped face, and two phosphorus donor ligands mutually *trans*. Crystals of the complex prepared by us were shown to be isomorphous with the earlier ones. The orthorhombic unit cell parameters we determined were $a = 27.981(4)$, $b = 12.378(6)$, $c = 12.952(6)$ Å, and $V = 4486(1)$ Å³.

The stereochemical positions of the PEt_3 ligands in the zero-valent molybdenum complex were also confirmed by single crystal X-ray analysis. This $\text{trans-Mo}(\text{CO})_4(\text{PEt}_3)_2$ species comprised only ca. 15% of the CO-containing products, and was the kinetically-controlled isomer. While it is true that the *trans* isomer is also the thermodynamically more stable one, isomerization of an initially produced *cis* form would not have been rapid enough under the reaction conditions to account for the isomeric distribution noted [8]. Presumably, reduction of the metal atom by carbon monoxide is accompanied by COCl_2 production. Both $\text{Mo}(\text{CO})_3(\text{PEt}_3)_2\text{Cl}_2$ and $\text{trans-Mo}(\text{CO})_4(\text{PEt}_3)_2$ are believed to be primary products of the reaction of carbon monoxide with $\text{Mo}_2\text{Cl}_4(\text{PEt}_3)_4$. Subsequent reaction processes, such as $\text{Mo}(\text{CO})_3(\text{PEt}_3)_2\text{Cl}_2$ with CO to afford $\text{Mo}(\text{CO})_4(\text{PEt}_3)_2$, were ruled out by the proper control experiments. Additionally, it is known that further reactions of $\text{Mo}(\text{CO})_4(\text{PR}_3)_2$ species with CO can lead to $\text{Mo}(\text{CO})_5\text{PR}_3$ and eventually $\text{Mo}(\text{CO})_6$ [10].

The reactions of $\text{W}_2\text{Cl}_4(\text{PEt}_3)_4$ and $\text{M}_2\text{Cl}_4(\text{P}^n\text{Bu}_3)_4$ ($\text{M} = \text{Mo}, \text{W}$) with CO yielded results virtually identical with those just described for $\text{Mo}_2\text{Cl}_4(\text{PEt}_3)_4$,

except that, as anticipated, dimer disruption in the W—W quadruply-bonded species occurred with greater facility than in their molybdenum analogues. A strong phosphine ligand dependence in the reactions of $M_2Cl_4(PR_3)_4$ derivatives with carbon monoxide under the mild reaction conditions employed was observed, e.g., $Mo_2Cl_4(PMe_3)_4$ and $Mo_2Cl_4(diphos)_2$ were unreactive. Studies of the reactivity of these derivatives with CO under more forcing conditions are underway. The infrared spectral data presented for an otherwise uncharacterized reaction of $Mo_2Cl_4(PEt_3)_4$ with CO at 52 atm in toluene at ambient temperature indicate the occurrence of processes that are consistent with the observations described herein [11].

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