A Mild Synthesis for Tetrakis-donor-substituted Molybdenum Carbonyls

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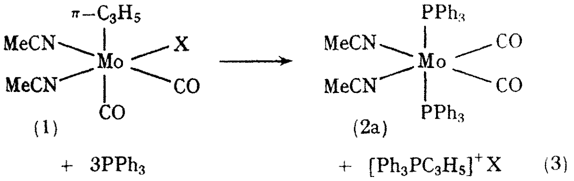
Summary Reaction of halogenobisacetonitrile-π-allyldicarbonylmolybdenum complexes with triphenylphosphine yields thermally unstable bisacetonitriledicarbonylbis(triphenylphosphine)molybdenum(0), in which acetonitrile is easily replaced to form a series of reactive dicarbonylmolybdenum(0) complexes.

RECENTLY we reported a very efficient synthesis for π-allyldicarbonylmolybdenum complexes (1), in which acetonitrile is easily replaced by, *e.g.*, pyridine, 2,2′-bipyridyl *etc* [1]

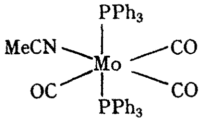
Treatment of (1) with triphenylphosphine in alcohol or acetonitrile at room temperature for 1 hr., or at 80° for 5 min., produces a new dicarbonylmolybdenum complex (2a) which crystallizes from the reaction mixture, and which contains no allylic function. From the filtrate allyltriphenylphosphonium halide (3) is isolated:[2]

This highly reactive complex bisacetonitrile dicarbonylbis(triphenylphosphine)molybdenum, is of great value for the low-temperature synthesis of other carbonyl complexes. Tetrasubstituted molybdenum(0) carbonyls have previously been prepared by thermal reactions from $Mo(CO)_6$ or $L_2Mo(CO)_4$ with chelating agents like 2,2'bipyridyl,[3] diphosphino- or diarsino-alkanes,[4,5] and ligands with appreciable π-acceptor capacity,[6] or (by Behrens' method) in liquid ammonia.[7]



(1) (2a) (3)

The properties of (2a) demonstrate why such complexes are not accessible by thermal reaction: it disproportionates when heated above 80° in common solvents, to give molybdenum and the tricarbonyl (4), while in the presence of alkylating agents like benzyl chloride the corresponding *cis*-tricarbonyl (5) is isolated. Prolonged heating in dimethyl sulphoxide gives the tetracarbonyl (6), which is also obtained when a suspension of (2a) is stirred under an atmosphere of carbon monoxide at normal temperature and pressure.



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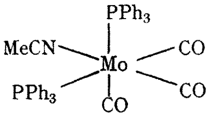

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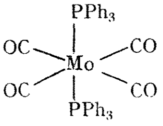
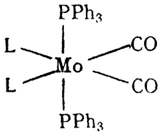
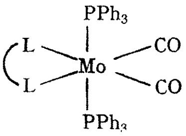


(6)

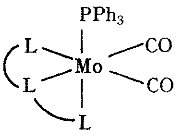
Similar reactions are observed with other complexes of type (2) or (7), obtained by nucleophilic exchange reactions.



(2)



(7)



(8)

Complex (2a) reacts with most mono-, bi-, and terdentate ligands to form complexes (2), (7), and (8): (see Table).

Thus, reaction of (2a) provides an interesting new route to highly substituted, thermally unstable molybdenum dicarbonyls. Except for the very sensitive (7f) good analytical results have been obtained.

Under mild conditions the positions *trans* to the carbonyl groups are substituted; (2c), (2d), and (7a—f) are formed at room temperature, while temperatures of about 70° are suitable for the synthesis of (2b), (2e), (7g), and (8). Solutions of these compounds are unstable in contact with air, but the crystalline compounds are fairly stable.

Carbonyl stretching frequencies of tetrasubstituted molybdenum carbonyls ($cm.^{-1}$)

No.	Ligand(s) L	Colour	CO frequencies	
(2a)	Acetonitrile	yellow	1813	1743
(2b)	Benzonitrile	red	1818	1760
(2c)	Pyridine	orange	1805	1736
(2d)	Isopropyl isocyanide	light yellow	1853	1805
(2e)	Dimethylformamide	orange yellow	1792	1703
(7a)	2,2'-Bipyridyl	dark green	1788	1718
(7b)	*o*-Phenanthroline	dark blue	1805	1730
(7c)	Pyridine aldoxime	dark green	1808	1728
(7d)	Biacetyl dioxime	blue violet	1828	1744
(7e)	Benzil monohydrazone	blue green	1869	1773
(7f)	Camphorquinone	green	1858	1818
(7g)	Ethylenediamine	yellow	1820	1682
(8)	Diethylenetriamine	yellow	1764	1660

All dicarbonyl complexes described here show two carbonyl absorptions of equal intensity, indicating their *cis*-arrangement. Most compounds show a third band of very low intensity at higher frequency than the A_1 mode. As repeated recrystallisation does not change the intensity ratios, this band is attributed to one of the aromatic overtone bands in this region having gained some intensity from resonance interaction. In view of the poor π-acceptor properties of several ligands in the $L_2L_2'\,Mo(CO)_2$ species the low carbonyl frequencies are not surprising. In (8), CO bond orders are reduced to such an extent that the average absorption frequency falls into the region associated with normal organic ketones, but "ketonic" reactions have not yet been performed successfully.

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[1] H. tom Dieck and H. Friedel, *J. Organometallic Chem.*, 1968, **14**, 375.

[2] A comparable "reduction" is that of $C_5H_5Mo(CO)_3Cl$ with Bu_3P, giving *inter alia* $[Bu_3P\text{-cp}]^+Cl^-$, described by A. J. Hart-Davis, D. J. Jones, R. J. Mawby, and C. White, (Proceedings, 1st International Symposium on New Aspects of the Chemistry of Metal Carbonyls and Derivatives, *Inorg. Chim. Acta*, Proc. C 3, Venice, Italy, Sept. 1968).

[3] H. Behrens and N. Harder, *Chem. Ber.*, 1964, **97**, 426, 433; L. W. Houk and G. R. Dobson, *J. Chem. Soc.* (*A*), 1966, 317; L. W. Houk and G. R. Dobson, *Inorg. Chem.*, 1966, **5**, 2119.

[4] J. Chatt and H. R. Watson, *J. Chem. Soc.*, 1961, 4980; F. Zingales and F. Canziani, *Gazzetta*, 1962, **92**, 343.

[5] H. L. Nigam, R. S. Nyholm, and M. H. B. Stiddard, *J. Chem. Soc.*, 1960, 1803.

[6] M. Lenzi and R. Poilblanc, *Compt. rend.*, 1966, **263**, *C*, 674.

[7] H. Behrens, E. Lindner, and J. Rosenfelder, *Chem. Ber.*, 1966, **99**, 2745.