# Reactions of Tris(dimethylamido)(π-cyclopentadienyl)titanium with Chromium, Molybdenum, and Tungsten Hexacarbonyls

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IN continuation of earlier work involving the reactions of metal dialkylamides with metal carbonyls,[1] we have found that tris(dimethylamido)-(π-cyclopentadienyl)titanium (independently discovered as reported by Chandra and Lappert[2]) reacts with $M(CO)_6$ (M = Cr, Mo, or W) in cyclohexane under u.v. irradiation forming black microcrystalline compounds whose elemental analyses conform to the general formula $(C_5H_5)Ti(NMe_2)_3M(CO)_3$. The carbonyl content was confirmed directly by the iodine in pyridine method. These compounds were less readily hydrolysed than $(C_5H_5)Ti(NMe_2)_3$ but could not be sublimed *in vacuo*; they decomposed above 190° without melting. Their solubility in benzene allowed the determination of molecular weights (cryoscopically), and their i.r. and n.m.r. spectra. Since these molecular weights agreed with the formula weight it was supposed that the molecular structure involved three bridging dimethylamido-groups joining the titanium and Group VI metals which were terminally bonded to the π-cyclopentadienyl group and three carbonyls respectively. The CO-stretching region (see Table) gave two intense bands as required by the $C_{3v}$ symmetry point group of the $M(CO)_3$ unit in agreement with this structure. However, the n.m.r. spectrum (see Table) although confirming the ratio of three dimethylamido-groups per cyclopentadienyl showed that the former were in four different magnetic environments and could not be reconciled with the proposed structure.

| M in $(C_5H_5)Ti(NMe_2)_3M(CO)_3)$ | I.r. bands[a] | N.m.r. spectrum[b]<br>$C_5H_5$-protons | <br>$Me_2N$-protons |
|---|---|---|---|
| Cr | 1918, 1835 | −344·4(5) | −141(3), −162(6),<br>−165·6(6), −180(3) |
| Mo | 1928, 1837 | −346·2(5) | −139·2(3), −165(6),<br>−169·2(6), −181·8(3). |
| W | 1925, 1835 | −343·8(5) | −132(3), −168(3),<br>−171·6(6), −173·4(6). |

[a] In benzene solution (cm.$^{-1}$);
[b] At 60 Mc./sec. in $C_6D_6$, chemical shifts in c./sec. relative to internal tetramethylsilane with relative intensities in parentheses.

The i.r. spectrum also shows bands characteristic of the π-cyclopentadienyl group but the assignment of bands in the metal–nitrogen stretching region[3] (500—600 cm.$^{-1}$) is uncertain due to the possible presence of metal–carbon (ring) stretching and MCO bending modes; the hydrolytic stability suggests that all dimethylamido-groups are bridging. The presence of only two CO-stretching bands appears to rule out alternative structures which could fit the n.m.r. spectrum. A further interesting feature is the relatively high frequencies of the CO-stretching bands compared with trisubstituted Group VI carbonyls containing aliphatic nitrogen donors[4] which suggests either that the nitrogen σ-donor character of the $TiNMe_2$ groups is decreased due to $\overset{-}{Ti}{=}\overset{+}{N}Me_2$ π-bonding or that the *d*-electrons of M are drawn into the vacant *d*-orbitals of the titanium by dative metal–metal bonding. It is interesting to compare these results both with those obtained by Abel *et al.*[5] on the compounds $MeSi(AsMe_2)_3M(CO)_3$ where M = Cr or Mo and especially with the work of Schmid, Nöth, and Deberitz on $(Me_2N)_3B,W(CO)_3$.[6]

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