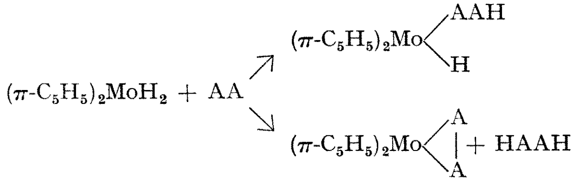
Reactions of Dihydridobis-(π-cyclopentadienyl)molybdenum. Substitution and Insertion Reactions at the Metal–Hydride Bonds

By SEI OTSUKA,* A. NAKAMURA, and H. MINAMIDA

(*Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka, Japan*)

Summary The metal–hydride bond in $(\pi\text{-}C_5H_5)_2MoH_2$ undergoes either insertion or substitution depending upon the π-acidity of the attacking reagent.

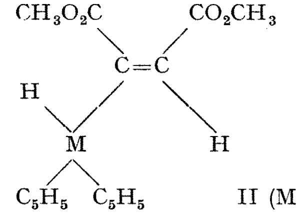
THE hydridic character of the second- and third-row transition-metal hydrides such as $(\pi\text{-}C_5H_5)_2MH_2$ (M=Mo, W) and $(\pi\text{-}C_5H_5)_2ReH$ is well known[1] and $(\pi\text{-}C_5H_5)_2MoH_2$ even behaves as a base, forming a BF_3 adduct.[2] We report the behaviour of $(\pi\text{-}C_5H_5)_2MoH_2$ (I) toward π-acids, *e.g.* acetylenes and azo-compounds, which can be summarized in two general reactions:



$$(\pi\text{-}C_5H_5)_2MoH_2 + AA \nearrow (\pi\text{-}C_5H_5)_2Mo\begin{cases}AAH\\H\end{cases} \quad (1)$$

$$(\pi\text{-}C_5H_5)_2MoH_2 + AA \searrow (\pi\text{-}C_5H_5)_2Mo\begin{cases}A\\|\\A\end{cases} + HAAH \quad (2)$$

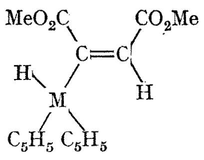
The insertion (addition) reaction of acetylenes with metal hydrides leading to σ-alkenylmetal compounds (equation 1) has been known for some time.[3-6] We have observed a remarkable stereochemical contrast between kinetically controlled addition reactions of (I) to acetylenedicarboxylate and to perfluorobut-2-yne. Thus, the reaction of (I) with dimethyl acetylenedicarboxylate takes place readily at 0° in tetrahydrofuran, affording solely a monomeric adduct (II),†, m.p. 103—105°, as deep red diamagnetic crystals (40%). Similarly, dimethyl acetylenedicarboxylate and $(\pi\text{-}C_5H_5)_2WH_2$ produced a deep red adduct (III)†, m.p. 103—105°. The structural assignments of (II) and (III) were based primarily on the i.r. and n.m.r. spectra which are comparable to those of the analogous *cis*-adduct $(\pi\text{-}C_5H_5)_2Re[C(CO_2Me)=CH(CO_2Me)]$.[5] In contrast, the addition of (I) to $CF_3C:CCF_3$ under comparable reaction conditions afforded exclusively a *trans*-adduct (IV), m.p. 112—113°, as was the case for the addition of $HMn(CO)_5$[4] or $HRe(CO)_5$[5] to $CF_3C:CCF_3$. This is concluded from the ^{19}F n.m.r. spectrum (in CS_2) which consists of four resonances



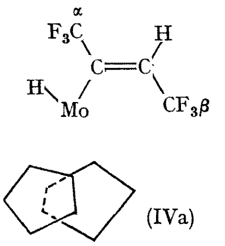
II (M=Mo), III (M=W)

---

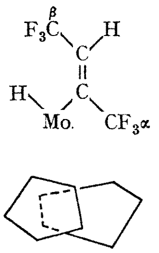
† Molecular weight measurements and elemental analysis agreed well with the calculated values.



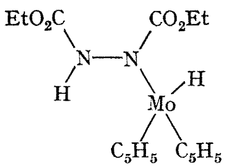
(II) M=Mo
(III) M=W



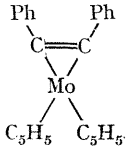
(IVa)



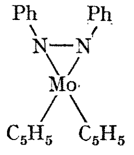
(IVb)



(V)



(VI)



(VII)

centred at (δ, p.p.m. from $CFCl_3$) 58·5 [double quartet, 2·9F, $J(\beta\text{-}CF_3\text{–}H)$ 9, $J(CF_3\text{–}CF_3)$ 2 Hz.], 59·0 [quintuplet, 2·9F $J(\alpha\text{-}CF_3\text{–}H)$ 2 Hz.], 60·0 (double quartet with the same coupling constants observed at δ 58·5, 3·1F), and 65·5 (quintuplet with the same coupling constants observed at δ 59·0, 3·1F) indicating a mixture of two non-geometrical isomers in a molar ratio of 9 : 10. The observed small coupling constant $J(CF_3\text{–}CF_3)$ of 2 Hz indicates a *trans*-configuration[4,5] of the double bond in both isomers. The ^1H n.m.r. spectrum shows a pair of resonances of approximately equal intensity for the vinyl, cyclopentadienyl, or hydride protons corresponding to the two isomers. The isomerism must result from the hindered rotation around the Mo–C bond. (The temperature-dependent ^1H n.m.r. spectrum will be described separately.) This seems to be the first reported example of conformational isomerism in σ-alkenyl complexes.

Thermal decomposition of the adduct (II) or (III) produced, instead of the expected olefin, the original acetylenedicarboxylate, whereas $CF_3C \vdots CCF_3$ could not be recovered from the thermal decomposition of (IV).

A concerted addition mechanism[3] implies a preferred *cis*-configuration for the adduct. The formation of a *trans*-adduct would require a multi-step mechanism involving an intermediate adduct.

Similar insertion takes place in the reaction of (I) with diethyl azodicarboxylate in ethanol at room temperature, affording an adduct (V), m.p. 135° (dec.), as yellow crystals.

Weaker π-acids, such as diphenylacetylene or azobenzene react with (I) rather sluggishly, in boiling toluene or tetrahydrofuran, substituting the two hydride ligands to give dark red crystals (VI),† m.p. 164—165°, or deep red crystals (VII)† m.p. 155—157°. Compounds (VI) and (VII) are thermally stable but air-sensitive. Their i.r. and n.m.r. data are consistent with the structures shown, as is their lack of reaction with 1,2-diphenylphosphinoethane. The type of co-ordination of azobenzene in (VII) is previously unknown, but similar co-ordination of azodicarboxylate was found in $IrCl(CO)(PPh_3)_2(RO_2CN{=}NCO_2R)$.[7]

Attempted reactions of $(\pi\text{-}C_5H_5)_2WH_2$ with diphenylacetylene or azobenzene failed to give a substitution product analogous to (VI) or (VII).

(*Received, August 5th,* 1969; *Com.* 1204.)

[1] A. P. Ginsberg, "Transition Metal Chemistry", ed. R. L. Carlin, Marcel Dekker, New York, 1965, vol. 1.
[2] D. F. Shriver, *J. Amer. Chem. Soc.*, 1963, **85**, 3509.
[3] M. Dubeck and R. A. Schell, *Inorg. Chem.*, 1964, **3**, 1757.
[4] P. M. Treichel, E. Pitcher, and F. G. A. Stone, *Inorg. Chem.*, 1962, **1**, 511.
[5] J. B. Wilford and F. G. A. Stone, *Inorg. Chem.*, 1965, **4**, 93.
[6] J. Trocha-Grimshaw and H. B. Henbest, *Chem. Comm.*, 1968, 757.
[7] M. Green, R. B. L. Osborn, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 3083.