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Preliminary communication

The preparation and reactions of some divalent derivatives of di-π-cyclopentadienylmolybdenum and -tungsten

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SUMMARY

A convenient route is described to divalent complexes of the type $(\pi\text{-}C_5H_5)_2ML$ where M = Mo or W and L = olefin or carbon monoxide; the complexes have basic properties.

Treatment of the dichlorides $(\pi\text{-}C_5H_5)_2MCl_2$ (I), M = Mo or W, with excess ethylaluminium dichloride in benzene or toluene results in a smooth reaction and the ethylene hydride cations $[(\pi\text{-}C_5H_5)_2MH(C_2H_3R)]^+$ (II) R = H, M = Mo or W may be readily isolated as their hexafluorophosphate salts in ca. 50% yields. The infrared spectra of the complexes are consistent with the proposed structures, and their ^1H NMR spectra show signals at τ15.0 (R = H, M = Mo) and τ16.58 (R = H, M = W) characteristic of protons directly bound to a transition metal.

In the reaction of the dichloride $(\pi\text{-}C_5H_5)_2MoCl_2$ with ethylaluminium dichloride, the neutral complex $(\pi\text{-}C_5H_5)_2MoCl(C_2H_5)$ is also formed and may be converted into complex (II) with R = H, M = Mo, by treatment with ethylaluminium dichloride in benzene or thallium tetrafluoroborate in acetone. Similarly, treatment of the dichloride (I), M = W with excess of isopropylmagnesium bromide in ether/benzene yields the propene analogue (II), R = Me, M = W, in 30% yield. The cations (II) are similar in behaviour to the trihydrides $[(\pi\text{-}C_5H_5)_2MH_3]^+$ (M = Mo or W) insofar that treatment with base (potassium hydroxide, ca. 1 *M*) causes abstraction of a proton and the neutral olefin complexes $(\pi\text{-}C_5H_5)_2M(C_2H_3R)$ (III) R = H, M = Mo and W; R = Me, M = W, are isolated in 90% yield. Tentative assignment of the C=C stretching frequency in the infrared may be made, and are as follows: R = H, M = Mo, ν(C=C) 1465 cm^{-1}; R = H, M = W, ν(C=C) 1430 cm^{-1}; R = Me, M = W, ν(C=C) 1450 cm^{-1}. The complexes (III) are readily reprotonated with aqueous hexafluorophosphoric acid, reforming the cations (II) quantitatively.

This route to divalent compounds of the type $(\pi\text{-}C_5H_5)_2ML$ may be extended to the facile preparation of the recently-described[1] carbonyl $(\pi\text{-}C_5H_5)_2Mo(CO)$. The carbonyl hydride cations $[(\pi\text{-}C_5H_5)_2MoH(CO)]^+$ (IV) is readily prepared, as a yellow crystalline compound, in 80% yield by treatment of the amine hydride cation $[(\pi\text{-}C_5H_5)_2MoH(NH_2CH_3)]^+$ [2] in acetone with carbon monoxide. On treatment with base, compound (IV) yields the neutral, divalent monocarbonyl $(\pi\text{-}C_5H_5)_2Mo(CO)$ in 80% yield $\nu(C{\equiv}O)$ 1905 cm^{-1}, parent ion *m/e* 256 corresponding to $(\pi\text{-}C_5H_5)_2\,{}^{98}Mo(CO)^+$.

The olefin complexes (III) are thermally stable at room temperature, but decompose *in vacuo* at 156° (R = H, M = Mo), 176° (R = H, M = W) and 114° (R = Me, M = W). They are especially resistant to olefin displacement by other two-electron ligands for example, the ethylene complex (III) R = H, M = Mo is recovered unchanged from triphenylphosphine melts at 90° after 36 h. Reactions with methyl iodide indicate that oxidative addition occurs to give products of stoichiometry $[(\pi\text{-}C_5H_5)_2M(C_2H_2R)Me]^+ I^-$. However the olefin ligands in the cationic complexes (II) R = H, M = Mo and W; R = Me, M = W, complex (II) R = H, M = Mo, in refluxing acetone with carbon monoxide gives the corresponding carbonyl hydride (IV) R = H, M = Mo in good yield. The reaction with the tungsten analogue (II) R = H, M = W, proceeds much more slowly.

In contrast, treatment of complexes (II) R = H, M = Mo and W; R = Me, M = W, with triphenylphosphine in refluxing acetone causes an internal insertion reaction and the triphenylphosphine alkyl derivatives $[(\pi\text{-}C_5H_5)_2M(PPh_3)(CH_2CH_2R)]^+$ (V) R = H, M = Mo; R = Me, M = W are formed in good yield. It is interesting to note that the ^1H NMR spectrum of complex (V) R = Me, M = W, indicates that only the n-propyl isomer is formed.

REFERENCES

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