Chelate Mn-C and Re-C σ-Bonded Complexes formed by Hydrometallation of an Olefinic Tertiary Phosphine

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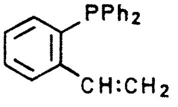
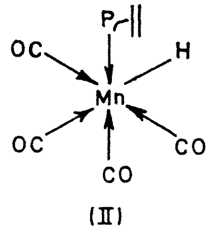
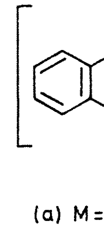
Summary The complex hydrides formed by *o*-styryldiphenylphosphine (sp), $HM(CO)_4(sp)$ (M = Mn or Re), rapidly undergo intramolecular hydride addition to the free vinyl group of the ligand giving stable chelate M–C σ-bonded complexes, the direction of addition being predominantly Markownikoff in the case of manganese and anti-Markownikoff in the case of rhenium.

THE reaction of transition-metal hydridocarbonyls with olefins to give metal alkyls is an important step in postulated mechanisms of hydrogenation, hydroformylation, and isomerisation of olefins using metal carbonyl complexes as catalysts. However, the metal alkyls cannot usually be isolated except when the olefin bears strongly electron-withdrawing substituents such as fluorine.[1] We have investigated the reaction of some metal hydridocarbonyls with the potentially bidentate olefinic ligand *o*-styryldiphenylphosphine, $o\text{-}CH_2{:}CH{\cdot}C_6H_4{\cdot}PPh_2$ (sp; I) in the hope that stable alkyls would be formed.





(II)



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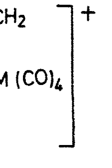

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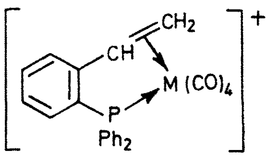

(V)

(a) M = Mn
(b) M = Re

Reaction of $HMn(CO)_5$ with (I) at 35° in n-pentane gives initially $HMn(CO)_4(sp)$ (II), isolated in 40% yield, which contains an unco-ordinated vinyl group. The ν(CO) bands at 2073(s), 1988(vs), 1971(vs), and 1961(vs) cm^{-1} (n-pentane) are similar in position to those of $HMn(CO)_4(PPh_3)$,[2] and the doublet at δ $-7{\cdot}34$ p.p.m. (J_{PH} 35·2 Hz) in the n.m.r. spectrum in C_6D_{12} solution indicates a probable *cis*-disposition of co-ordinated hydrogen and phosphorus. On heating in cyclohexane under nitrogen, the hydride isomerises to give a mixture of chelate Mn–C σ-bonded complexes, formed by addition of Mn–H to the free vinyl group. The total yield of alkyls based on hydride is *ca.* 40%, some insoluble paramagnetic material also being formed. The predominant isomer (IIIa), comprising 80—90% of the total product, contains a five-membered ring arising from Markownikoff addition, and the minor component (IVa) contains a six-membered ring arising from anti-Markownikoff addition. These cannot be separated, but are readily recognised by their distinctive proton n.m.r. spectra [(IIIa) ($CDCl_3$) : δ 1·77 (d, 3H, CH_3, J_{HH} 7·3 Hz) and 3·40 p.p.m.

(q of d, 1H, C*H*, J_{HH} 7·3 Hz, J_{PH} 2·5 Hz); (IVa) ($CDCl_3$) δ 1·35 (m, 2H, CH_2) and 2·95 p.p.m. (m, 2H, CH_2)]. The yield of alkyls increases to *ca.* 70% if (II) is heated in CO, which suggests that the first step is loss of CO from (II) accompanied by co-ordination of the double bond, to give $HMn(CO)_3$(sp). Hydride addition followed by uptake of CO should then give the alkyls quantitatively, but in the absence of CO, net decomposition must occur.

The reaction of $HRe(CO)_5$ with (I) at 35° gives initially the hydride $HRe(CO)_4$(sp) (detectable only by its i.r. spectrum), but this rapidly isomerises to give the six-membered Re–C σ-bonded chelate complex (IVb) as the only product, [n.m.r. ($CDCl_3$): δ 1·30 (m, 2H, CH_2, J_{PH} 2·2 Hz); 3·24 p.p.m. (m, 2H, CH_2, small J_{PH})]. A difference in the direction of addition of $HMn(CO)_5$ and $HRe(CO)_5$ to an olefin has been noted previously using $CF_2:CFCl$.[3] In our system, the difference may be related to the fact that $HRe(CO)_5$ is a weaker acid than $HMn(CO)_5$,[4] so that addition in the sense H^+–M^- will be favoured for the lighter element. We are currently investigating the direction of addition of (I) to other transition metal hydrides. The addition of (I) to $PtHCl(PPh_3)_2$ to give a chelate Pt–C σ-bonded complex has recently been reported,[5] but the direction of addition could not be established with certainty.

In contrast to simple $RMn(CO)_5$ complexes (R = alkyl or aryl), which readily undergo substitution with ligands such as CO, tertiary phosphines, and phosphites giving acyls [$RCOMn(CO)_4$(ligand)],[6,7] the chelate complexes (IIIa), (IVa) (mixture), and (IVb) are recovered unchanged after treatment with CO (70°, 100 atm., 5 days), or with triphenyl phosphite in C_6H_6 at 70° for 5 days. This remarkable inertness to substitution provides additional support for the view that acyl formation from $RMn(CO)_5$ proceeds *via* alkyl group migration,[6,7] since this cannot readily occur in the chelate complexes.

The reagent $Ph_3C^+BF_4^-$ readily removes hydride ion from the alkyl chain of complexes (IIIa), (IVa) (mixture) and from (IVb) giving the chelate olefinic cations $[M(CO)_4(sp)]^+$ (M = Mn or Re) (V) identical with those obtained by reaction of $M(CO)_5Cl$ with (I) in the presence of $AlCl_3$.[8] Hydride ion reduction ($NaBH_4$/THF) of the rhenium cation (Vb) gives the five-membered chelate Re–C σ-bonded complex (IIIb) which could not be obtained from $HRe(CO)_5$ and (I) [n.m.r. ($CDCl_3$): δ 1·98 (d, 3*H*, CH_3, J_{HH} 7·3 Hz) and 3·35 p.p.m., (q of d, 1H, C*H*, J_{HH} 7·3 Hz, J_{PH} 4·0 Hz)]. This series of reactions is analogous to the isomerisation of π-$C_5H_5Fe(CO)_2CH_2CH_2CH_3$ to the corresponding isopropyl derivative by successive hydride ion abstraction and addition.[9]

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