π-Allylnickel Halides containing Tertiary Phosphines and Carbon Monoxide as Ligands and their Reaction with Acetylene and Carbon Monoxide

By F. GUERRIERI and G. P. CHIUSOLI*
(Laboratori di Chimica Organica Esplorativa, Montecatini-Edison Co., Novara, Italy)

IN the attempt to elucidate the mechanism of the substitutive carbonylation of allylic halides,[1] we have isolated new nickel complexes, probably penta-co-ordinated,† whose composition is in agreement with the formula

$$[\pi\text{-}C_3H_5\cdot Ni(CO)(PR_3)X] \text{ (I)},$$

where R is alkyl or aryl and X is Cl, Br, or I.

These complexes are easily prepared starting either from $[\pi\text{-}C_3H_5\cdot Ni(PR_3)X]$ (II),[2] in a benzene–methanol or toluene–methanol solution (9 : 1 in volume) and adding carbon monoxide at room temperature or treating $[Ni(CO)_3PR_3]$ (III)[3] with an allyl halide in the above solution. Air-sensitive crystals separate.

Complex $[\pi\text{-}C_3H_5\ Ni(CO)(PPh_3)I]$ (IV) is an orange, diamagnetic solid showing typical i.r. and n.m.r. absorptions (i.r. in Nujol, metal carbonyl band at 2040 cm.$^{-1}$; n.m.r. in $CDCl_3$, 100 Hz., Me_4Si as internal standard: π-allyl signals centred at τ 5·03; 6·07 and 6·72). Complex (IV) is in equilibrium in solution with $[\pi\text{-}C_3H_5\cdot Ni(PPh_3)I]$ (V), as shown by (V) slowly separating from solutions of (IV) in benzene–hexane. Complex $[\pi\text{-}C_3H_5\cdot Ni(CO)(PPh_3)Br]$ (VI) is also an orange diamagnetic solid. Complex $[\pi\text{-}C_3H_5\cdot Ni(CO)(PBu_3)I]$ (VII) crystallizes on cooling below −20°.

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† This problem is being investigated by Prof. Bassi of Istituto Donegani, Milano.

Treatment of complex (VI) or (IV) at 0° and atmospheric pressure with a 70:30 CO:C_2H_2 mixture in toluene–methanol solution (8:2 in volume) results in the formation of methyl *cis*-hexa-2,5-dienoate (47%):

$$\text{(VI)} + \text{CH}\equiv\text{CH} + 3\text{CO} + \text{MeOH}$$
$$\rightarrow \text{CH}_2{=}\text{CH–CH}_2\text{–CH}{=}\text{CH–CO}_2\text{Me} + \text{Ni(CO)}_3\text{(PPh}_3) + \text{HBr}$$

Other reaction products[1] and nickel bromide are also obtained.

Under the same conditions complexes of type (II) give acetylene polymers unless they are previously transformed into (I) by absorption of 1 mole of carbon monoxide. Both complexes (I) and (II) give mainly acetylene polymers on addition of another molecule of triphenylphosphine (no CO evolved) before the gases are introduced into the solution.

To explain these results, we assume that acetylene displaces the π-allylic group from one co-ordination site giving rise to a σ-allylic group such as the reactive species which are able to attack acetylene itself and carbon monoxide in (I). If such an arrangement of ligands is not possible owing to the presence of another ligand (*e.g.*, a second molecule of triphenylphosphine), the formation of methyl hexadienoate is prevented.

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