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Preliminary communication

π-Cyclopentadienyls of nickel(II)
XII. Nickel containing bidentate ligands: preparation of π-C_5H_5 Ni-μ-SC_6H_5 $\cdot\mu$($Ph_2PCH_2PPh_2$)Mo(CO)$_4$ and π-C_5H_5 Ni-μ-CN$\cdot\mu$($Ph_2PCH_2PPh_2$)Mo(CO)$_4$

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SUMMARY

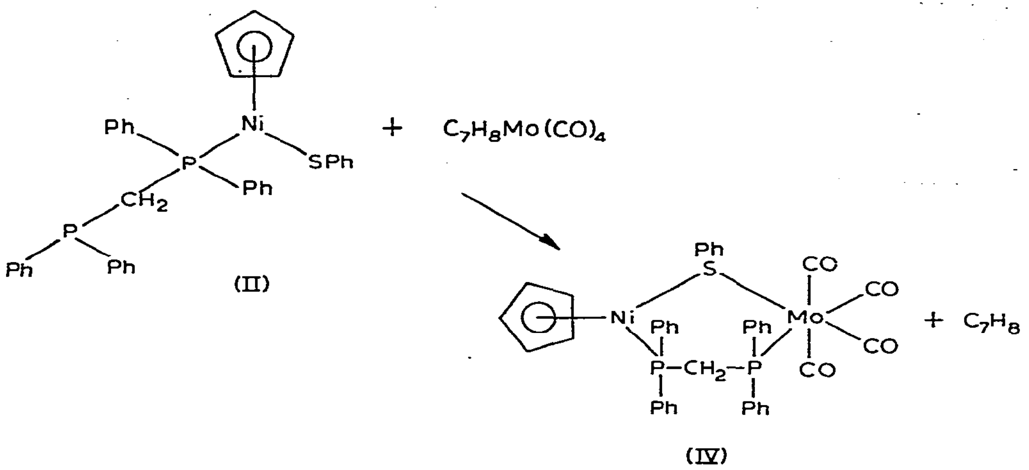
π-$C_5H_5NiPPh_2CH_2PPh_2SC_6H_5$ and π-$C_5H_5NiPPh_2CH_2PPh_2CN$ act as bidentate ligands and produce π-C_5H_5Ni-μ-SPh-μ-($PPh_2CH_2PPh_2$)Mo(CO)$_4$ and π-C_5H_5Ni-μ-CN-μ-($PPh_2CH_2PPh_2$)Mo(CO)$_4$, respectively, on treatment with norbornadienemolybdenum tetracarbonyl.

Recently π-$C_5H_5NiPPh_2CH_2PPh_2CN$ (I) was prepared by treatment of [π-$C_5H_5NiPPh_2CH_2PPh_2$]$^+Cl^-$ with aqueous NaCN[1]. By analogy, the product π-$C_5H_5NiPPh_2CH_2PPh_2SPh$ (II) would be expected from the reaction between [π-$C_5H_5NiPPh_2CH_2PPh_2$]$^+Cl^-$ and NaSPh[2]. Complexes (I) and (II) are interesting because they can act as metal-containing ligands.

Green and his colleagues[3] reported recently that dithio derivatives of the type (π-C_5H_5)$_2$M(SR)$_2$ (M = Ti, Mo, W, Cr and Nb) act as bidentate ligands to transition metals and give mixed metal compounds such as (π-C_5H_5)$_2$M-μ-(SR)$_2$Mo(CO)$_4$. Brown *et al.*[4] also reported the preparation of mixed metal compounds by using the ligand [π-C_5H_5Fe(CO)$_2$PPh$_2$(CH$_2$)$_n$PPh$_2$]$^+$ in which the bis-tertiary-phosphine donor sites are not used.

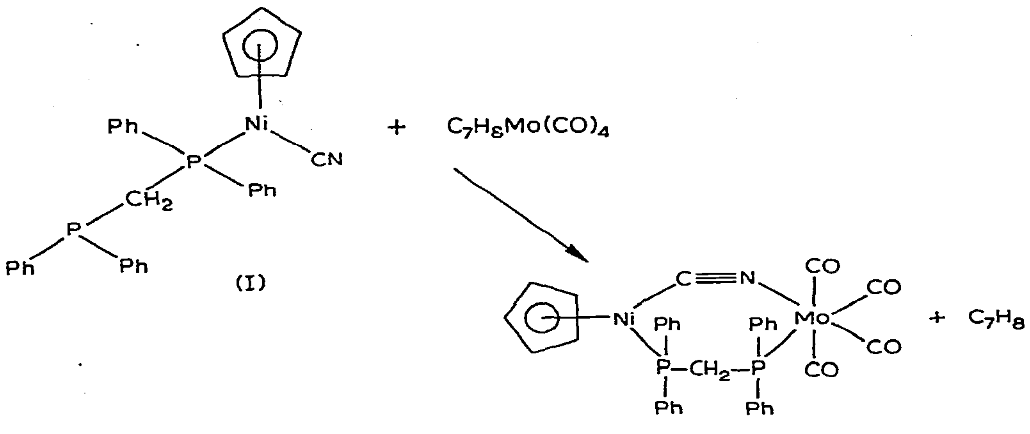
We have now shown that (I) and (II) act as bidentate ligands, and give π-C_5H_5Ni-μ-(CN)-μ-($PPh_2CH_2PPh_2$)Mo(CO)$_4$ (III) and π-C_5H_5Ni-μ-(SPh)-μ-($PPh_2CH_2PPh_2$)Mo(CO)$_4$ (IV) respectively on reaction with norbornadiene molybdenum tetracarbonyl. On addition of an ether solution of (II) to an ether solution of C_7H_8Mo(CO)$_4$, a black precipitate was formed in high yield. Recrystallization from benzene–n-hexane gave black crystals with the empirical formula

π-$C_5H_5NiSPhPPh_2CH_2PPh_2Mo(CO)_4$ (IV) m.p. 162°C (dec.) (Found: C, 57.69; H, 3.87; S, 3.50. $C_{40}H_{32}MoNiO_4P_2S$ calcd.: C, 58.21; H, 3.88; S, 3.89%) The molecular weight (cryoscopy in benzene) was 740 ± 50 (calcd. 825), indicating that (IV) was monomeric in benzene. From the IR and NMR spectra it was deduced that the product was tetracarbonyl-[μ-phenylthio-μ-methylenebis(diphenylphosphine)-π-cyclopentadienylnickel] molybdenum, *i.e.* complex (IV)



The four carbonyl stretching IR bands at 2009, 1912, 1885 and 1855 cm^{-1} of (IV) indicate that complex (II) coordinates to *cis* positions of the $Mo(CO)_4$ moiety[5]. The proton NMR spectrum of (IV) in C_6D_6 shows bands at τ 1.9–3.3 associated with the phenyl protons, a singlet at τ 5.13 due to the π-cyclopentadienyl protons and a triplet at τ 6.95 due to the methylene protons of methylenebis(diphenylphosphine). The ^{31}P NMR spectrum shows two doublets at δ −27.6 and −31.4 ppm (PPh_3 as external reference) (J(P–P); 30.4 Hz), and this indicates the presence of non-equivalent phosphorous atoms, *i.e.* one is coordinated to nickel and the other is coordinated to molybdenum.

Similar reaction of (I) with $C_7H_8Mo(CO)_4$ gave the reddish brown crystals (III) m.p. 182°C (dec.). Elemental analysis, the IR spectrum, and the ^1H and ^{31}P NMR spectra supported structure (III). The IR spectrum of (III) shows, in addition to the four bands at 2037, 1917, 1895 and 1843 cm^{-1} which are characteristic for the *cis*-disubstituted $Mo(CO)_4$ moiety, a sharp C≡N stretching frequency at 2150 cm^{-1} which is 20 cm^{-1} higher than that of (I). It is well known that bridging cyanide groups exhibit a higher absorption frequency than do terminal cyanide groups[6], so there seems little doubt that (I) is coordinated to molybdenum by the uncoordinated phosphorous atom of $Ph_2PCH_2PPh_2$ and the lone pair of the nitrogen of the CN group.



(I)

(III)

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