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Preliminary communication

MOLECULAR STRUCTURE OF π-$C_5H_5NiFe(CO)_3Ph_3PC{\equiv}CH$

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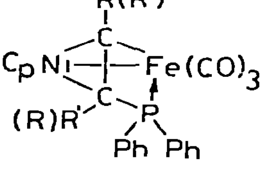
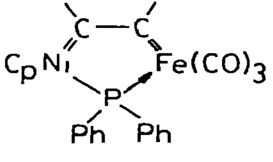
Summary

The mixed metal complex π-$C_5H_5NiFe(CO)_3Ph_3PC{\equiv}CH$, obtained from the reaction of π-$C_5H_5Ni(PPh_3)C{\equiv}CH$ with $Fe_2(CO)_9$, is shown by an X-ray diffraction study to contain the ethynyltriphenylphosphonium group as the bridging ligand. Based on this structure, new reactions of $[Ph_3PC{\equiv}CPh]Br$ with some organometallic compounds have been attempted from which π-$C_5H_5NiFe(CO)_3(Ph_3PC_2Ph)$ and $CoFe(CO)_6(Ph_3PC_2Ph)$ can be obtained.

Transition metal acetylide complexes are of interest as a source for new mixed transition-metal clusters [1-3]. In a previous communication [2], we observed that π-$C_5H_5Ni(PPh_3)C{\equiv}CR$ reacts with $Fe_2(CO)_9$ to give new mixed metal complexes with the compositions π-$C_5H_5Ni(PPh_3)(C_2R)Fe(CO)_3$ (Ia, R = Ph; Ib, R = CO_2CH_3; Ic, R = n-C_4H_9; Id, R = H). Ia, Ib and Id have the same compositions as the complexes II (IIa, R,R' = Ph; IIb, R = CO_2CH_3, R' = Ph; IId, R = H, R' = Ph) obtained from the reaction of μ-carbonyl-μ-diphenylphosphido-π-cyclopentadienylnickel tricarbonyliron with $RC{\equiv}CR'$ [4]. For II, a structure III was first given erroneously by us, but later Kruger determined structure IIa by X-ray crystallography [5]. The present complexes I are different from complexes of type II in their physical properties, therefore, it was of interest to elucidate the structure of I.



(II)(a R,R'=Ph)



(III)

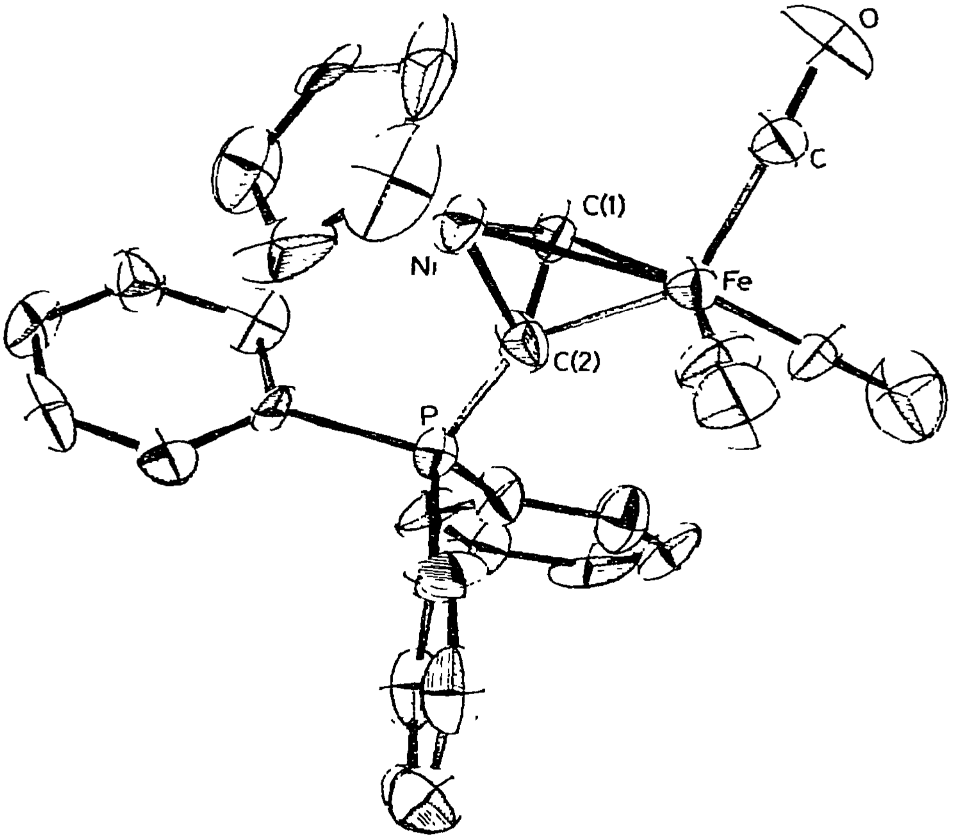
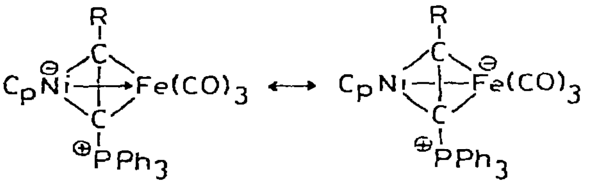


Fig 1 Perspective view of the molecule Id.

Crystals of Id belong to the monoclinic space group $P2_1/c$. The unit cell data are a = 10.674, b = 12.294, c = 20.351 Å, β = 110.13°; U = 2507.34, Z = 4, and D_x = 1.460 g/cm^3. The crystal was mounted on a Rigaku four-circle atomated diffractometer with the a axis coincident with the diffractometer ϕ axis. Using Zr-filtered Mo-K_α radiation, the data were collected, out to 2θ = 50° using the $2\theta-\omega$ scan technique with a scan speed of 4°/min. The structure was solved by the heavy atom method and refined by the block-diagonal matrix least-squares technique. The R value was 0.094 for 1961 reflections with $F_o^2 \geqslant 3\sigma(F_o^2)$. A view of the molecule is given in Fig. 1.

The bond distances of the Ni—Fe (2.420(4)), Ni—C(1) (1.93(2)), Ni—C(2) (1.93(2)), Fe—C(1) (1.98(2)), Fe—C(2) (1.94(2)), and C(1)—C(2) (1.37(3) Å) bonds show that the acetylene moiety coordinates on the nickel and iron atoms as an usual bridged type similar to that seen in the complexes $(C_5H_5)_2Ni_2PhC{\equiv}CPh$ [6] and $Co_2(CO)_6PhC{\equiv}CPh$ [7]. The bond distance of the C(1)—C(2) is very similar to that of the dinickel complex (1.35 Å).

The most striking feature of the molecular structure is the environment of the tetra-substituted phosphorus atom. The angle P—C(2)—Ni (127°) is significantly smaller than the angle P—C(2)—Fe (148°), which shows that the phosphorus atom is placed closer to the nickel atom than to the iron atom.



(A) (B)

Thus, the structure of I can be proposed as an intramolecular salt type (A and B) with the formal negative charge on the nickel or on the iron atom as shown. If the charge is localized on the nickel atom as in A, the charge may cause the angle distortion. On the other hand, the shortest C—C intermolecular distance of 3.46(3) Å between the $Fe(CO)_3$ end and the phenyls bound to phosphorus is still less than the shortest C—C intermolecular distance of 3.62(3) Å between the NiCp end and the phenyls bound to phosphorus although the Ni—C—P angle is less than the Fe—C—P. The distance 3.46 Å may not be much longer than the distance of Van der Waals contact of two carbons if the value of 1.7 Å is taken as half the thickness of a phenyl ring [8]. Thus it appears as though the angle distortion may be chiefly the result of steric hindrance. Some intramolecular salt type mononuclear complexes with a phosphonium group are known [9-12] and the structures of $(OC)_4BrMnC_2$-PPh_3 [13] and $(OC)_3MoC_3H_5PPh_3$ [14] have been determined.

The structure containing the $Ph_3P^+C{\equiv}CR$ moiety led us to examine the reaction of $[Ph_3PC{\equiv}CPh]Br$ [15] with some organometallic compounds. The treatment of the phosphonium salt with $(C_5H_5)_2Ni$ and $Fe_2(CO)_9$ in THF at room temperature for a week followed by chromatography through a silica gel column using C_6H_6 as eluent gave Ia in reasonable yield. Similarly, from the reaction of $Co_2(CO)_8$ and $Fe_2(CO)_9$ with the phosphonium salt, another new mixed metal complex of the composition, $CoFe(CO)_6Ph_3PC_2Ph$, could also be obtained, which probably has a structure similar to that of I.

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