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Preliminary communication

SYNTHESIS AND STRUCTURE OF π-ACETYLENE COMPLEXES OF ZERO-VALENT IRON AND NICKEL: *sym*-DI-μ-PHENYLDIPHENYLPHOSPHINOACETYLENE-BIS {TRICARBONYLIRON(0)} AND *sym*-DI-μ-t-BUTYLDIPHENYLPHOSPHINOACETYLENE-BIS {CARBONYLNICKEL(0)}

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Iron and nickel carbonyls oligomerize acetylenes so readily that very few simple acetylene complexes of these metals have been characterized [1, 2]. Complexes of the type $(RC{\equiv}CR')Fe(CO)_4$ are said to be highly reactive and can only be isolated* when R and R′ are bulky substituents, such as $C(CH_3)_3$ and $Si(CH_3)_3$ [2]. In only one case did the reaction of $Ni(CO)_4$ with acetylenes yield a stable π-alkyne derivative, $Ni_4(CO)_3(CF_3C_2CF_3)_3$ [3]. A few nickel analogs of the platinum complexes $(Ph_3P)_2Pt(RC{\equiv}CR')$ have been synthetised from $Ni(C_2H_4)(PR_3)_2$ [4, 5], but the complexes are reportedly [5] too unstable for an analysis. In contrast, we have found that phosphinoacetylenes, $Ph_2PC{\equiv}CR$, react with either $Fe_2(CO)_9$ or $Ni(CO)_4$ to give stable Fe^0 and Ni^0 π-alkyne complexes. These simple π-alkyne complexes are possible models for the intermediates in the iron [2] and nickel carbonyl [6] catalyzed oligomerization of acetylenes. Therefore, X-ray structural studies of $Fe_2(CO)_6(Ph_2PC{\equiv}CPh)_2$ and $Ni_2(CO)_2$-$(Ph_2PC{\equiv}CBu\text{-}t)_2$ were undertaken since there is a lack of X-ray data for simple, non-bridging, π-acetylene complexes of 1st row transition metals.

The reaction of $Fe_2(CO)_9$ with $Ph_2PC{\equiv}CPh$ in benzene at room temperature gives the σ,π-acetylide complex $Fe_2(CO)_6(C{\equiv}CPh)(PPh_2)$ as the major product, together with smaller quantities of $Fe_2(CO)_6(Ph_2PC_2Ph)_2$ (I). The yellow-brown air stable complex I has $\nu(C{-}O_{terminal})$ bands at 2020s, 2012s, 1988s, 1970s (br), 1940s (br) cm^{-1}, bands of medium intensity at 1805 and 1798 cm^{-1} but no $\nu(C{\equiv}C)$ bands of the free ligand**. The reaction of $Ni(CO)_4$ with $Ph_2PC{\equiv}CBu$-t in carefully degassed non-polar solvents at room temperature gives $Ni_2(CO)_2$-

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[*] Details on the characterization and properties of these compounds have never been published.
[**] Bands near 1800 cm^{-1} in I and II are due to $\nu(C{\equiv}C)$ of the coordinated acetylenes.

$(Ph_2PC_2Bu\text{-}t)_2$ (II). A strong IR band was observed at 1810 cm^{-1} similar to that found in the iron complex, together with $\nu(CO_t)$ bands at 1980 and 1938 cm^{-1}. The $\nu(C{\equiv}C)$ of the ligand was also absent.

Crystal data: $Fe_2(CO)_6(Ph_2PC{\equiv}CPh)_2$, mol. wt. 852.4, monoclinic crystals, space group $P2_1/n$; a = 12.032, b = 19.155, c = 17.644 Å, β 91.39°; U = 4065.2, D_m = 1.42 g/cm^3, Z = 4, D_c =.1.393 g/cm^3. $Ni_2(CO)_2(Ph_2PC{\equiv}CBu\text{-}t)_2$, mol. wt. 706.1, monoclinic crystals, $P2_1/n$; a = 16.733, b = 12.233, c = 19.677 Å, β 118.31°; U = 3546.0, D_m = 1.32 g/cm^3, Z = 4, D_c = 1.324 g/cm^3. The structures were solved by the heavy atom method and refined by least-squares techniques. The current R value for I is 0.065 for the 3400 reflections with $I \geqslant 1.8\sigma(I)$ measured with graphite monochromatized Mo-K_α radiation. For II the R value is 0.070 for 2268 reflections, with $I \geqslant 2.0\sigma(I)$ measured with Ni-filtered Cu-K_α radiation. All measurements were made with the $P\bar{1}$ diffractometer using a variable speed scan technique.

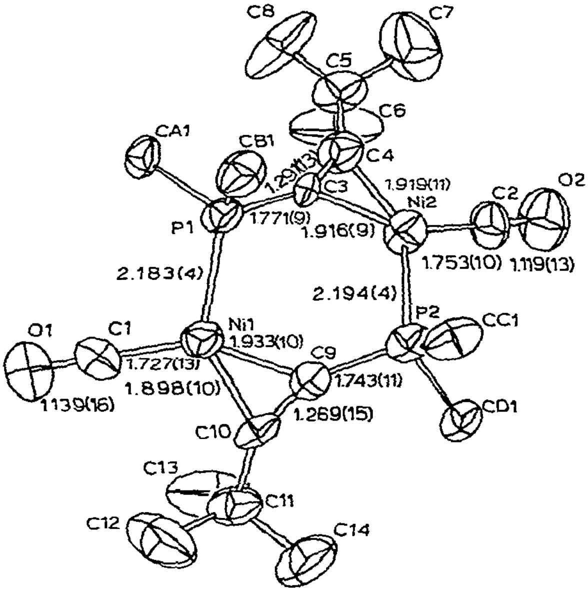

Fig. 1. A view of the molecular structure of $Ni_2(CO)_2(Ph_2PC_2Bu\text{-}t)_2$ showing the atomic numbering and pertinent distances and angles. Only one carbon atom of each phenyl ring is shown.

The nickel complex shown in Fig. 1 is the first example of a simple acetylene complex obtained from the reaction of $Ni(CO)_4$ and an acetylene. The closely related iron complex is shown in Fig. 2. Pertinent bond distances and angles are shown in these figures. In both binuclear complexes the metal atoms are coordinated to the phosphorus atom of one phosphinoacetylene and the triple bond of the second phosphinoacetylene. The iron atoms in I can be considered to be the centers of trigonal bipyramids if the alkynes are assumed to occupy one site in the trigonal plane. In II, the nickel atoms are the centers of trigonal planar arrangements, consisting of the CO group, the phosphorus atom, and the alkyne moiety. The angle between the planes Ni(1), P(1), C(1) and Ni(1),

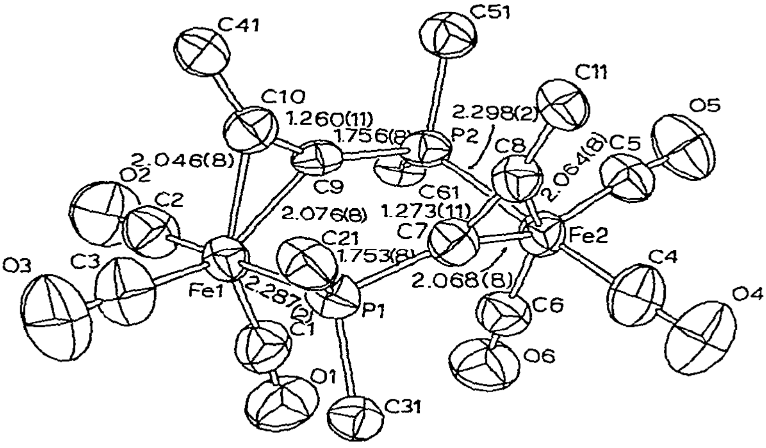

Fig. 2. A view of the molecular structure of $Fe_2(CO)_6(Ph_2PC_2Ph)_2$ showing the atomic numbering and pertinent distances and angles. For the sake of clarity only one carbon atom of each phenyl ring is shown.

C(9), C(10) is 6.0° and between Ni(2), P(2), C(2) and Ni(2), C(3), C(4) is 5.9°. The orientations of the alkynes follow the pattern found in other zerovalent metal—olefin and acetylene complexes [7—9].

The strength of the metal acetylene interaction is reflected in a lengthening of $C{\equiv}C$ from 1.20 Å in "free" acetylene to 1.267(11) Å in I and 1.280(14) Å in II. The iron—acetylene π-interaction is clearly stronger than in $Fe_2(CO)_6(C{\equiv}CPh)(PPh_2)$ [10], where $C{\equiv}C$ is 1.232(10) Å, as indicated by the shorter Fe—C distances of 2.063(8) Å in I versus 2.125(8) and 2.304(7) Å in $Fe_2(CO)_6(C{\equiv}CPh)(PPh_2)$. Similarly, the Ni—C distances in II, av. 1.914(10) Å, are significantly shorter than the Ni—C bond distances of 2.02(2) Å in $Ni(\pi\text{-}C_2H_4)[(o\text{-}CH_3C_6H_4O)_3P$ [8] and 1.99(1) Å in $Ni(\pi\text{-}C_2H_4)(PPh_3)_2$ [9] but comparable to the Ni—C distance of 1.911(12) Å in the acrylonitrile complex $Ni(H_2C{=}CHCN)[(o\text{-}CH_3\text{-}C_6H_4O)_3P]_2$ [8]. The latter complex is particularly interesting since acrylonitrile is one of the few olefins which react directly with $Ni(CO)_4$ to yield stable olefin complexes. The Ni—C bond in II is apparently one of the strongest Ni—C (π-bond) interactions reported to date.

Whereas I can be considered as a disubstituted derivative of $Fe(CO)_5$, the compounds $[Ni(CO)(Ph_2PC{\equiv}CR)]_2$ are rare and unusual examples of coordinatively unsaturated carbonyl complexes of Ni^0. Complexes of the types I and II may be of considerable utility in organometallic chemistry because of their facile synthesis and ease of handling, their similarity to intermediates, such as $Fe(CO)_4(RC{\equiv}CR)$ and $Ni(PR_3)_2(R'C{\equiv}CR'')$, proposed for acetylene trimerization reactions [1, 2, 6] and the presence of groups susceptible to both nucleophilic and electrophilic attack. We are currently exploring the use of phosphinoacetylenes for the synthesis of other metal—acetylene complexes of low stability.

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