to Dr. N. Sutin for several helpful discussions.

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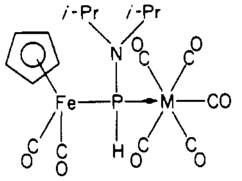
Synthesis of Heterobimetallic Complexes from Metal Carbonyl Complexes of Bis(diisopropylamino)phosphine

Sir:

Recently we reported[1] the facile and selective cleavage of one diisopropylamino group from the bis(diisopropylamino)phosphine metal carbonyl complexes ($(i\text{-}Pr_2N)_2PHM(CO)_n$ (i-Pr = isopropyl; $n = 5$, M = Cr, Mo, and W; $n = 4$, M = Fe) with hydrogen halides HX (X = Cl and Br) to give the corresponding metal carbonyl complexes $i\text{-}Pr_2NP(H)XM(CO)_n$. We have now found that reactions of these latter complexes with the strongly nucleophilic[2] metal carbonyl anion $CpFe(CO)_2^-$ provide a route to novel heterobimetallic complexes containing a bridging $i\text{-}Pr_2NPH$ phosphido group having potentially reactive P–H and P–N bonds. The complexes initially formed in such reactions in at least three cases undergo facile single decarbonylation reactions with formation of a heteronuclear metal–metal bond. These complexes therefore provide a direct indication of the effects of metal–metal bond formation on the properties of phosphido complexes. Related heterobimetallic diphenylphosphido chemistry, involving however totally different preparative methods, was reported in 1971 by Yasufuku and Yamazaki.[3]

A tetrahydrofuran solution of $NaFe(CO)_2Cp$ freed from excess sodium amalgam[4] was treated at −78 °C with a stoichiometric amount of $i\text{-}Pr_2NP(H)XM(CO)_5$ (M = Cr, X = Br; M = Mo and W, X = Cl). After the mixture was stirred overnight at room temperature, the solvent was removed in vacuum. The residue was extracted with pentane. Filtration, concentration, and cooling the pentane extracts gave orange-brown crystals of the corresponding $CpFe(CO)_2P(H)(N\text{-}i\text{-}Pr_2)M(CO)_5$ derivative (Table I).

These complexes appear to have structures I (M = Cr, Mo, W) containing an intact $CpFe(CO)_2$ unit and no heteronuclear metal–metal bond. Their infrared spectra in the ν(CO) region (Table I) exhibit no bridging carbonyl frequencies, and among the terminal carbonyl frequencies, two (e.g., those at 1970 and 1920 in $CpFe(CO)_2P(H)(N\text{-}i\text{-}Pr_2)Cr(CO)_5$) can be assigned to the $CpFe(CO)_2$ unit, with the pattern of the remaining ν(CO) frequencies corresponding to that expected for the $M(CO)_5$ group. A property of $CpFe(CO)_2P(H)(N\text{-}i\text{-}Pr_2)W(CO)_5$ (I, M = W) of chemical interest is the cleavage of its remaining diisopropylamino group by hydrogen halides HX (X = Cl and Br) in hexane solution to give the corresponding brown crystalline derivatives $CpFe(CO)_2PHXW(CO)_5$ (II, X = Cl and Br).



I

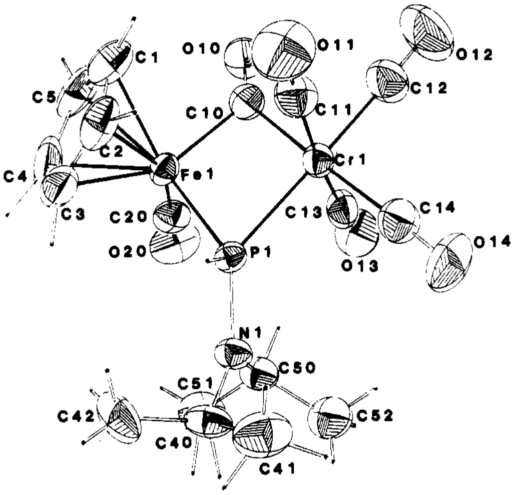
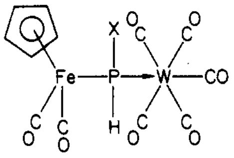
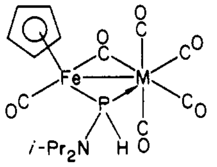


Figure 1. ORTEP diagram of the complex $CpFeCr(CO)_6P(H)(N\text{-}i\text{-}Pr_2)$ (III, M = Cr).



II



III

The most interesting chemical property of the complexes $CpFe(CO)_2P(H)(N\text{-}i\text{-}Pr_2)M(CO)_5$ (M = Cr and W) is their facile photochemical decarbonylation to give the corresponding complexes $CpFeM(CO)_6P(H)(N\text{-}i\text{-}Pr_2)$, shown by X-ray crystallography to have structures III (M = Cr and W) containing a heteronuclear metal–metal bond.[5] Thus a red-orange pentane solution of $CpFe(CO)_2P(H)(N\text{-}i\text{-}Pr_2)M(CO)_5$ becomes deep brown after only 5 min of ultraviolet irradiation. Evaporation of solvent from the filtered pentane solution after 10 min of irradiation followed by recrystallization from hexane gave black $CpFeCr(CO)_6P(H)(N\text{-}i\text{-}Pr_2)$. The structure III (M = Cr) of this complex was suggested by the observation of a bridging ν(CO) frequency at 1811 cm^{-1} (Table I) in addition to several terminal ν(CO) frequencies. This unusual structure was subsequently confirmed by X-ray diffraction. Our initial infrared spectra of the tungsten analogue $CpFeW(CO)_6P(H)(N\text{-}i\text{-}Pr_2)$ failed to exhibit its bridging ν(CO) frequency. We therefore also determined the structure of $CpFeW(CO)_6P(H)(N\text{-}i\text{-}Pr_2)$ by X-ray diffraction. After this structure determination indicated that $CpFeW(CO)_6P(H)(N\text{-}i\text{-}Pr_2)$ had structure III (M = W) completely analogous to $CpFeCr(CO)_6P(H)(N\text{-}i\text{-}Pr_2)$, we reran the infrared spectrum in much more concentrated solution and found the expected bridging ν(CO) frequency around 1800 cm^{-1}, which was much weaker than that of its chromium analogue.

The structures of $CpFeM(CO)_6P(H)(N\text{-}i\text{-}Pr_2)$ (M = Cr and W) indicate that the iron is bonded to a terminal carbonyl group and pentahapto bonded to a cyclopentadienyl ring and that the other metal M is bonded to four terminal carbonyl groups. The iron and M atoms are within bonding distances (Fe–Cr = 2.733 (2) Å in $CpFeCr(CO)_6P(H)(N\text{-}i\text{-}Pr_2)$ and Fe–W = 2.827 (4) Å in $CpFeW(CO)_6P(H)(N\text{-}i\text{-}Pr_2)$). These metal–metal bonds are bridged by a carbonyl group (Fe–C = 2.023 (9), Cr–C = 2.023

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(5) The compounds $FeMC_{17}H_{20}O_6NP$ (M = Cr and W) are isomorphous, forming monoclinic crystals of space group $P2_1/c$ with $Z = 4$. For M = Cr: $a = 14.362$ (5) Å, $b = 7.733$ (2) Å, $c = 19.244$ (8) Å, $\beta = 104.00$ (3)°, $V = 2073.8$ (12) Å^3, $D_{calcd} = 1.515$ g/cm^3. For M = W: $a = 14.491$ (5) Å, $b = 7.808$ (2) Å, $c = 19.456$ (8) Å, $\beta = 103.17$ (3)°, $V = 2143.6$ (12) Å^3, $D_{calcd} = 1.874$ g/cm^3. Data (5734 points for M = Cr and 5929 points for M = W) were collected at room temperature by using molybdenum Kα radiation ($\lambda = 0.71069$ Å), a variable scan rate, a θ–2θ scan mode, and a scan width of 1.2° below Kα_1 and 1.2° below Kα_2 to a maximum 2θ value of 116°. Data were corrected for Lorentz, polarization, and background effects. After removal of redundant data and space group forbidden data, 2414 (M = Cr) and 2271 (M = W) reflections were considered observed [$I > 3.0\sigma(I)$]. The final agreement factors, R, after successive least-squares/different Fourier cycles were 5.3% for M = Cr and 6.8% for M = W.

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Table I. Heterobimetallic Compounds with Phosphido Bridges Containing a Phosphorus-Hydrogen Bond[a]

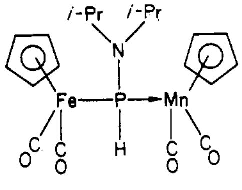
			^{31}P NMR[d]		^{1}H NMR[d]		
compd[b]	yield, %	IR ν(CO) freq,[c] cm^{-1}	δ(P)	$\lvert ^1J(\text{PH})\rvert$, Hz	δ(P-H)	$\delta(C_5H_5)$	$\delta(CH_3)$
		(A) Compounds without a Metal-Metal Bond					
$CpFe(CO)_2P(H)(N\text{-}i\text{-}Pr_2)Cr(CO)_5$	73[e]	2040 w, 2005 m, 1970 s, 1955 w, 1935 s, 1920 s	62.6	295	7.31	5.04	1.23
$CpFe(CO)_2P(H)(N\text{-}i\text{-}Pr_2)Mo(CO)_5$	66[e]	2056 w, 2006 m, 1973 s, 1939 s, 1931 s	36.7	302	7.20	4.90	1.25
$CpFe(CO)_2P(H)(N\text{-}i\text{-}Pr_2)W(CO)_5$	69[e]	2060 w, 2010 m, 1970 s, 1945 s, 1935 m, 1920 s	6.7	310	7.57	4.98	1.22
$CpFe(CO)_2P(H)(N\text{-}i\text{-}Pr_2)Mn(CO)_2Cp$	63[e]	2001 s, 1956 s, 1928 s, 1874 s	98.7	306	7.7	4.9, 4.5	1.2
$CpFe(CO)_2PHClW(CO)_5$	57[f]	2069 w, 2038 m, 2003 m, 1954 s, 1948 s, 1933 s	89.9	290	7.72	5.17	none
$CpFe(CO)_2PHBrW(CO)_5$	43[f]	2069 w, 2037 m, 1995 m, 1940 s, 1935 s, 1925 s	63.7	286	6.82	5.18	none
		(B) Compounds with a Metal-Metal Bond					
$CpFeCr(CO)_6P(H)(N\text{-}i\text{-}Pr_2)$	53[g]	2031 m, 1963 s, 1959 s, 1926 s, 1811 m[h]	206.3	360	9.2	4.6	1.3
$CpFeW(CO)_6P(H)(N\text{-}i\text{-}Pr_2)$	52[g]	2047 m, 1968 s, 1952 s, 1931 s, 1810 vw[h]	159.8	363	9.9	4.6	1.3
$Cp_2FeMn(CO)_3P(H)(N\text{-}i\text{-}Pr_2)$	21[g]	1940 s, 1876 s, 1755 s[h]	224.8	347	*i*	4.6, 4.5	1.3

[a] All compounds in this table gave correct analyses for carbon, hydrogen, and nitrogen or halogen. [b] Cp = η^5-cyclopentadienyl, *i*-Pr = isopropyl. [c] These ν(CO) frequencies were measured in hexane or cyclohexane. [d] These NMR spectra were measured in $CDCl_3$ solution. [e] Yield from the $NaFe(CO)_2Cp$ + $i\text{-}Pr_2NP(H)XM(CO)_5$ or $i\text{-}Pr_2NP(H)XMn(CO)_2Cp$ reaction. [f] Yield from the $CpFe(CO)_2P(H)(N\text{-}i\text{-}Pr_2)W(CO)_5$ + HX reaction. [g] Yield from the photolysis of $CpFe(CO)_2P(H)(N\text{-}i\text{-}Pr_2)M(CO)_5$ or $CpFe(CO)_2P(H)(N\text{-}i\text{-}Pr_2)Mn(CO)_2Cp$. [h] Bridging ν(CO) frequency. [i] Paramagnetic impurities in solution prevented observation of the proton P-H resonance.

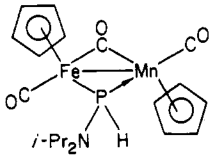
(7) Å in $CpFeCr(CO)_6P(H)(N\text{-}i\text{-}Pr_2)$ and Fe-C = 2.12 (3), W-C = 2.07 (2) Å in $CpFeW(CO)_6P(H)(N\text{-}i\text{-}Pr_2)$) and a $i\text{-}Pr_2NPH$ phosphido group (Fe-P = 2.207 (2), Cr-P = 2.292 (2) Å in $CpFeCr(CO)_6P(H)(N\text{-}i\text{-}Pr_2)$ and Fe-P = 2.201 (5), W-P = 2.433 (6) Å in $CpFeW(CO)_6P(H)(N\text{-}i\text{-}Pr_2)$). The bridging carbonyl group is symmetrical within experimental error despite the dissimilarity of the metal atoms being bridged.

Table I indicates substantial changes in various NMR parameters upon decarbonylation of I to III with heteronuclear metal-metal bond formation leading to a FePM three-membered ring. Most dramatic is the ~150 ppm downfield phosphorus-31 chemical shift upon conversion from I to III, which is undoubtedly a consequence of the ring formation. Also noticeable is a ~60 Hz increase in the $\lvert ^1J(\text{P-H})\rvert$ coupling constant and a ~2 ppm downfield proton chemical shift of the P-H hydrogen.

Related bimetallic compounds containing cyclopentadienylmanganese carbonyl units can also be prepared. Thus treatment of a hexane solution of $(i\text{-}Pr_2N)_2PHMn(CO)_2Cp$ with hydrogen chloride gives an 89% yield of yellow $i\text{-}Pr_2NP(H)ClMn(CO)_2Cp$ [infrared ν(CO) in cyclohexane, 1961 and 1901 cm^{-1}; phosphorus-31 NMR, δ 144.2 ($\lvert ^1J(\text{PH})\rvert$ = 373 Hz)]. Reaction of $i\text{-}Pr_2NP(H)ClMn(CO)_2Cp$ with $NaFe(CO)_2Cp$ in tetrahydrofuran gives deep red $CpFe(CO)_2P(H)(N\text{-}i\text{-}Pr_2)Mn(CO)_2Cp$, formulated as IV on the basis of its spectroscopic properties (Table I).



IV



V

Ultraviolet irradiation of IV in cyclohexane solution gives black $Cp_2FeMn(CO)_3P(H)(N\text{-}i\text{-}Pr_2)$ formulated as V because of the observation of a bridging ν(CO) frequency at 1755 cm^{-1} in its infrared spectrum.

The preliminary observations described in this communication suggest that the selective cleavage of diisopropylamino groups from metal carbonyl complexes of $(i\text{-}Pr_2N)_2PH$ can lead ultimately to a rich variety of interesting heterobimetallic derivatives. These derivatives contain potentially reactive phosphorus-nitrogen bonds in contrast to the numerous known diarylphosphido heterobimetallic derivatives such as $WIrH(\mu\text{-}PPh_2)_2(CO)_5(PPh_3)$,[6] $(OC)_4Mn(\mu\text{-}PR_2)(\mu\text{-}H)Mo(CO)_2Cp$ (R = *p*-tolyl),[7] $(OC)_5W(\mu\text{-}PPh_2)Re(CO)_4$,[8] and $Cp_2ZrW(\mu\text{-}PPh_2)_2(CO)_4$.[9]

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Supplementary Material Available: Listings of crystal data, positional parameters, anisotropic thermal parameters, bond angles, and bond distances in the two complexes $CpFeM(CO)_6P(H)(N\text{-}i\text{-}Pr_2)$ (M = Cr and W) and an ORTEP diagram of $CpFeW(CO)_6P(H)(N\text{-}i\text{-}Pr_2)$ (8 pages). Ordering information is given on any current masthead page.

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In Pursuit of the Active Site of Assimilatory Sulfite Reductases. Reactions of Ferric Porphyrin and $[Fe_nS_n(SPh)_4]^{2-}$ Complexes (n = 2, 4)

Sir:

Spectroscopic investigations of the catalytically active β subunit of *E. coli* NADPH-sulfite reductase have established that the two prosthetic groups at the active site, siroheme and an Fe_4S_4 cluster, are chemically linked.[1-7] Exchange interactions between these centers are observed in several different oxidation and ligation states of the enzyme and during substrate reduction. Similar

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