(Dialkylamino)phosphorus Metal Carbonyls. 11. Addition of the $(i\text{-}Pr_2NP)_2Fe_2(CO)_6$ Unit to C=O, C≡N, and C=C Multiple Bonds[1]

Y. W. Li, M. G. Newton, and R. B. King*

Department of Chemistry, University of Georgia, Athens, Georgia 30602

Received September 22, 1993®

Reactions of the olefinic aldehydes and ketones MeCH=CHO, PhCH=CHCOMe, 2-cyclohexanone, and $(Me_2C{=}CH)_2CO$ with the $(i\text{-}Pr_2NP)_2Fe_2(CO)_6$ unit generated by heating $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ in boiling toluene give the 1:1 adducts $[(i\text{-}Pr_2NP)_2OCHCH{=}CHMe]Fe_2(CO)_6$, $[(i\text{-}Pr_2NP)_2OCMeCH{=}CHPh]Fe_2(CO)_6$, $[(i\text{-}Pr_2NP)_2OCCH{=}CH(CH_2)_3]Fe_2(CO)_6$, and $[(i\text{-}Pr_2NP)_2OC(CH{=}CMe_2)_2]Fe_2(CO)_6$, respectively. The NMR spectra of these adducts indicate in all cases addition of the C=O double bond rather than a C=C double bond to the $(i\text{-}Pr_2NP)_2Fe_2(CO)_6$ unit. Reactions of maleic anhydride and phthalic anhydride with $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ in boiling toluene give $[(i\text{-}Pr_2NP)_2OCOCOCH{=}CH]Fe_2(CO)_6$ and $[(i\text{-}Pr_2NP)_2OCOCOC_6H_4]Fe_2(CO)_6$, respectively. The NMR spectra of these adducts indicate addition of one of the anhydride C=O bonds to the $(i\text{-}Pr_2NP)_2Fe_2(CO)_6$ unit. An X-ray diffraction study of the maleic anhydride adduct $[(i\text{-}Pr_2NP)_2OCOCOCH{=}CH]Fe_2(CO)_6$ (triclinic, $P\bar{1}$; $a = 9.679(6)$ Å, $b = 10.476(6)$ Å, $c = 15.440(3)$ Å, $\alpha = 75.23(9)°$, $\beta = 73.73(6)°$, $\gamma = 76.40(0)°$, $Z = 2$) supports this conclusion with the C–O distance of the complexed carbonyl group being 1.43(3) Å in contrast to the C=O distance of 1.30(4) Å of the uncomplexed carbonyl group. Reactions of the nitriles RCN (R = Me, Ph) with $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ lead to the corresponding adducts $[(i\text{-}Pr_2NP)_2N{=}CR]Fe_2(CO)_6$ (R = Me, Ph). An X-ray diffraction study of $[(i\text{-}Pr_2NP)_2N{=}CMe]Fe_2(CO)_6$ (monoclinic, $P2_1/m$, $a = 8.761(6)$ Å, $b = 14.362(6)$ Å, $c = 10.984(1)$ Å, $\beta = 100.75(6)°$, $Z = 2$) indicates addition of the $(i\text{-}Pr_2NP)_2Fe_2(CO)_6$ unit to the C≡N of the acetonitrile. However, an X-ray diffraction study on the adduct $[(i\text{-}Pr_2NP)_2CH_2CHC{\equiv}N]Fe_2(CO)_6$ obtained from acrylonitrile and $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ in boiling toluene (triclinic, $P\bar{1}$, $a = 8.783(2)$ Å, $b = 10.732(2)$ Å, $c = 15.753(2)$ Å, $\alpha = 70.99(2)°$, $\beta = 77.00(2)°$, $\gamma = 85.47(2)°$, $Z = 2$) indicates that the $(i\text{-}Pr_2NP)_2Fe_2(CO)_6$ unit has added to the C=C rather than the C≡N bond of the acrylonitrile. Reaction of ethyl cyanoacetate with $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ in boiling toluene gives an adduct shown by X-ray crystallography (monoclinic, Cc; $a = 18.211(1)$ Å, $b = 10.762(2)$ Å, $c = 16.434(1)$ Å, $\beta = 106.09(6)°$, $Z = 4$) to be $[(i\text{-}Pr_2NP)_2NH{=}C{=}CHCO_2Et]Fe_2(CO)_6$ derived from an imine tautomer of ethyl cyanoacetate with hydrogen bonding between the ester carbonyl and imine hydrogen. Reaction of norbornadiene with $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ in boiling toluene gives $(i\text{-}Pr_2NPH)(nor\text{-}C_7H_8P)Fe_2(CO)_6$ shown by X-ray diffraction (triclinic, $P\bar{1}$, $a = 7.783(7)$ Å, $b = 9.124(4)$ Å, $c = 17.635(8)$ Å, $\alpha = 98.67(4)°$, $\beta = 94.23(5)°$, $\gamma = 104.91(5)°$; $Z = 2$) to be a novel nortricyclane derivative arising from addition of norbornadiene to a phosphinidene–iron carbonyl intermediate, $(i\text{-}Pr_2NPH)(P)Fe_2(CO)_6$.

Introduction

One of the important reaction pathways of the readily available[2,3] phosphorus-bridging carbonyl derivative $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ (**I** in Figure 1) is the expulsion of its phosphorus-bridging carbonyl group upon heating in boiling toluene to give a reactive $(i\text{-}Pr_2NP)_2Fe_2(CO)_6$ unit. This unit was first trapped by treatment with alcohols (ROH: R = Me, Et) to give the adducts $(i\text{-}Pr_2NPOR)(i\text{-}Pr_2NPH)Fe_2(CO)_6$ (**IV** in Figure 1).[4] However, attempts to isolate a tetrahedrane $(i\text{-}Pr_2NP)_2Fe_2(CO)_6$ (**III** in Figure 1) by heating $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ (**I**) in boiling toluene in the absence of a trapping agent led instead to complete decomposition despite the fact that the related *tert*-butyl derivative $(t\text{-}BuP)_2Fe_2(CO)_6$ is a stable isolable compound.[5] The failure to isolate a stable tetrahedrane **III** from the pyrolysis of **I** suggests the following: (1) Reactions of the $(i\text{-}Pr_2NP)_2Fe_2(CO)_6$ unit formed by pyrolytic phosphorus-bridging carbonyl extrusion from **I** proceed through the diradical **II** (Figure 1) arising directly by breaking the two P–C bonds required for loss of the phosphorus-bridging carbonyl group. (2) Conversion of the paramagnetic diradical **II** to the diamagnetic diferradiphosphatetrahedrane $(i\text{-}Pr_2NP)_2Fe_2(CO)_6$ (**III** in Figure 1) by formation of a P–P bond is not a favored process; the diradical **II** in the absence of a reactive substrate decomposes completely without the formation of a stable organophosphorus iron carbonyl intermediate.

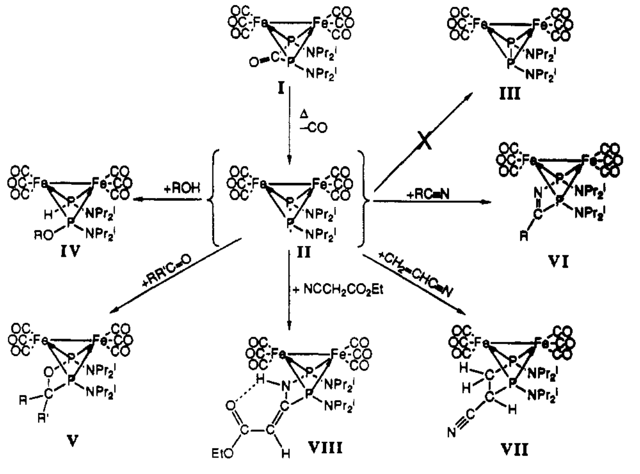


Figure 1. Proposed scheme for reactions of $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ involving loss of the phosphorus-bridging carbonyl group.

The first example of the addition of the $(i\text{-}Pr_2NP)_2Fe_2(CO)_6$ unit to multiple bonds was the report in 1991[1] of the reactions

---

® Abstract published in *Advance ACS Abstracts*, November 1, 1993.

(1) For part 10 of this series, see: King, R. B.; Bhattacharyya, N. K.; Holt, E. M. *J. Organomet. Chem.* **1991**, *421*, 247.
(2) King, R. B.; Wu, F.-J.; Sadanani, N. D.; Holt, E. M. *Inorg. Chem.* **1985**, *24*, 4449.
(3) King, R. B.; Wu, F.-J.; Holt, E. M. *J. Am. Chem. Soc.* **1987**, *109*, 7764.
(4) King, R. B., Wu, F.-J.; Holt, E. M. *J. Am. Chem. Soc.* **1988**, *110*, 2775.
(5) De, R. L.; Wolters, D.; Vahrenkamp, H. *Z. Naturforsch.* **1986**, *41b*, 283.

0020-1669/93/1332-5720$04.00/0

Table I. Products from Reactions of $(IpR_2NP)_2COFe_2(CO)_6$ with Unsaturated Organic Compounds

unsaturated organic compd	product	isolated yield (%)	mp (°C)	anal. (%): found (calcd) C	H	N
$MeCH{=}CHO$	$[(i\text{-}Pr_2NP)_2OCHCH{=}CHMe]Fe_2(CO)_6$	59	108–109	43.1 (43.2)	5.6 (5.6)	4.6 (4.6)
$PhCH{=}CHCOMe$	$[(i\text{-}Pr_2NP)_2OCMeCH{=}CHPh]Fe_2(CO)_6$	62	136–137	48.9 (48.9)	5.6 (5.6)	4.1 (4.1)
2-cyclohexenone	$[(i\text{-}Pr_2NP)_2OCCH{=}CH(CH_2)_3]Fe_2(CO)_6$	73	126–128	45.2 (45.2)	5.6 (5.7)	
$(Me_2C{=}CH)_2CO$	$[(i\text{-}Pr_2NP)_2OC(CH{=}CMe_2)_2]Fe_2(CO)_6$	67	155–157	47.6 (47.7)	6.1 (6.2)	4.1 (4.1)
maleic anhydride	$[(i\text{-}Pr_2NP)_2OCOCOCH{=}CH]Fe_2(CO)_6$	52	166–167	41.2 (41.3)	4.8 (4.7)	
phthalic anhydride	$[(i\text{-}Pr_2NP)_2OCOCOC_6H_4]Fe_2(CO)_6$	40	217–219	44.9 (45.2)	4.8 (4.7)	4.0 (4.1)
$MeC{\equiv}N$	$[(i\text{-}Pr_2NP)_2N{=}CMe]Fe_2(CO)_6$	40	163–165	41.3 (41.2)	5.3 (5.4)	7.2 (7.2)
$PhC{\equiv}N$	$[(i\text{-}Pr_2NP)_2N{=}CPh]Fe_2(CO)_6$	21	100–102	46.6 (46.5)	5.1 (5.2)	6.4 (6.5)
$CH_2{=}CHC{\equiv}N$	$[(i\text{-}Pr_2NP)_2CH_2CHC{\equiv}N]Fe_2(CO)_6$	62	157–159	42.5 (42.4)	5.3 (5.3)	7.0 (7.1)
$N{\equiv}CCH_2C(O)OEt$	$[(i\text{-}Pr_2NP)_2NH{=}C{=}CHCO_2Et]Fe_2(CO)_6$	58	166–167	42.1 (42.2)	5.3 (5.4)	6.5 (6.4)
norbornadiene	$[(i\text{-}Pr_2NPH)(nor\text{-}C_7H_8P)Fe_2(CO)_6$	24	123–125	42.7 (42.6)	4.5 (4.3)	2.7 (2.6)

Table II. Infrared ν(CO) Frequencies and Phosphorus-31 NMR Spectra of Compounds Derived from $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$

compd	infrared ν(CO) (cm^{-1})[a]	phosphorus-31 NMR (δ) $NPFe_2X$[a]	$NPFe_2C$	J(P–P) (Hz)
$(i\text{-}Pr_2NP)_2COFe_2(CO)_6$[c]	2060 m, 2016 s, 1996 s, 1975 s, 1964 m, 1720 m[d]	225.6 s	225.6 s	
$[(i\text{-}Pr_2NP)_2OCHPh]Fe_2(CO)_6$[e]	2054 m, 2010 s, 1992 s, 1964 s, 1952 m	296.1 d	221.2 d	116
$[(i\text{-}Pr_2NP)_2OCPh_2]Fe_2(CO)_6$[e]	2052 m, 2013 s, 1987 s, 1974 m, 1957 m	288.6 d	259.1 d	128
$[(i\text{-}Pr_2NP)_2OCHCH{=}CHMe]Fe_2(CO)_6$	2050 m, 2006 s, 1984 s, 1960 s, 1944 m	294.2 d	217.1 d	110
$[(i\text{-}Pr_2NP)_2OCMeCH{=}CHPh]Fe_2(CO)_6$	2051 m, 2004 s, 1980 s, 1963 s, 1940 m	284.8 d	248.9 d	128
$[(i\text{-}Pr_2NP)_2OCCH{=}CH(CH_2)_3]Fe_2(CO)_6$	2049 m, 2001 s, 1980 s, 1955 s, 1940 m	285.2 d	244.7 d	121
$[(i\text{-}Pr_2NP)_2OC(CH{=}CMe_2)_2]Fe_2(CO)_6$	2047 m, 2005 s, 1980 s, 1960 s, 1944 m	286.6 d	259.3 d	117
$[(i\text{-}Pr_2NP)_2OCOCOCH{=}CH]Fe_2(CO)_6$	2058 m, 2018 s, 1994 s, 1975 s, 1956 m	296.6 d	215.1 d	120
$[(i\text{-}Pr_2NP)_2OCOCOC_6H_4]Fe_2(CO)_6$	2059 m, 2017 s, 1993 s, 1975 s, 1955 m	298.2 d	221.1 d	127
$[(i\text{-}Pr_2NP)_2N{=}CMe]Fe_2(CO)_6$	2046 m, 2006 s, 1983 s, 1963 s, 1945 m	251.6 d	193.9 d	16
$[(i\text{-}Pr_2NP)_2N{=}CPh]Fe_2(CO)_6$	2047 m, 2008 s, 1983 s, 1965 s, 1949 m	253.1 d	203.7 d	17
$[(i\text{-}Pr_2NP)_2CH_2CHC{=}N]Fe_2(CO)_6$	2052 m, 2010 s, 1987 s, 1966 s, 1950 m	229.1 d[f]	216.2 d	51
$[(i\text{-}Pr_2NP)_2NH{=}C{=}CHCO_2Et]Fe_2(CO)_6$	2052 m, 2010 s, 1985 s, 1965 s, 1951 m	240.9 d	165.8 d	99
$[(i\text{-}Pr_2NPH)(nor\text{-}C_7H_8P)Fe_2(CO)_6$	2041 m, 2000 s, 1970 m, 1962 m, 1952 m	133.2 dd[g]	236.7 d	115

[a] X = N, O. [b] These infrared ν(CO) frequencies were measured in CH_2Cl_2 solution. Abbreviations: Me = methyl; *i*-Pr = isopropyl, Ph = phenyl. [c] Data from: King, R. B.; Wu, F.-J.; Holt, E. M. *J. Am. Chem. Soc.* **1987**, *109*, 7764. [d] Phosphorus-bridging carbonyl (P–C(O)–P) ν(CO) frequency. [e] Data from: King, R. B.; Bhattacharyya, N. K.; Holt, E. M. *J. Organomet. Chem.* **1991**, *421*, 247. [f] X = CH. [g] *i*-Pr_2NPH group: $|^1J(P\text{–}H)|$ = 380 Hz.

of the phosphorus-bridging carbonyl derivative $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ (I) with the aldehydes and ketones $RR'C{=}O$ (R = R′ = H, Ph; R = Ph, R′ = H, Me; R + R′ = $-(CH_2)_5-$) in boiling toluene to give products of the general type $[(i\text{-}PrNP)_2OCRR']Fe_2(CO)_6$ shown by X-ray diffraction on the benzaldehyde derivative (R = Ph, R′ = H) to have structure V (R = Ph, R′ = H; Figure 1) in which the $(i\text{-}Pr_2NP)_2Fe_2(CO)_6$ unit has added across the C=O of the aldehyde or ketone. We have now found that the $(i\text{-}Pr_2NP)_2Fe_2(CO)_6$ unit generated by pyrolysis of $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ can add to a much larger variety of carbon multiple bonds. This paper reports the first examples of additions of the $(i\text{-}Pr_2NP)_2Fe_2(CO)_6$ unit to C≡N and C=C bonds, examples of the addition of the $(i\text{-}Pr_2NP)_2Fe_2(CO)_6$ unit to the C=O bond in anhydrides and unsaturated ketones containing both C=O and C=C bonds as potentially reactive sites, and a novel norticyclane derivative $(i\text{-}Pr_2NPH)(nor\text{-}C_7H_8)Fe_2(CO)_6$ from the reaction of $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ (I) with norbornadiene. Structural determinations by X-ray diffraction are reported for the $(i\text{-}Pr_2NP)_2Fe_2(CO)_6$ adducts of acetonitrile, acrylonitrile, ethyl cyanoacetate, and maleic anhydride as well as the product from the reaction of $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ with norbornadiene.

Experimental Section

Microanalyses (Table I) were performed by the Atlantic Microanalytical Laboratory, Norcross (Atlanta), GA. Infrared spectra (Table II) were run in the 2200-1600-cm^{-1} metal carbonyl region in hexane solution and recorded on a Perkin-Elmer Model 1600 Fourier transform infrared spectrometer calibrated against polystyrene film. Phosphorus-31 (Table II), carbon-13 (Table III), and proton (Table IV) NMR spectra were run on a Bruker 300-MHz spectrometer with external 85% phosphoric acid, internal tetramethylsilane, and internal tetramethylsilane, respectively, as references. Carbon-13 and phosphorus-31 NMR spectra were normally run with proton decoupling. All chemical shifts (δ) are given downfield from the reference. The relaxation reagent $Cr(acac)_3$[6] was added to the carbon-13 NMR samples in order to obtain better spectra in the metal carbonyl region. Melting and decomposition points were taken in capillaries and are uncorrected.

The $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ (I) starting material was prepared from commercial $Fe(CO)_5$, PCl_3, and $i\text{-}Pr_2NH$ through $Na_2Fe(CO)_4{\cdot}1.5C_4H_8O_2$ and $i\text{-}Pr_2NPCl_2$ using the published procedure.[3,7] The organic substrates were obtained from standard commercial sources.

Before use, all solvents were distilled under dry nitrogen over appropriate drying agents (sodium benzophenone ketyl or metal hydrides except for chlorinated solvents). Air-sensitive organometallic and organophosphorus compounds were handled in a dry nitrogen atmosphere.

Reactions of $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ with Olefinic Ketones and Aldehydes. A mixture of 2.0 g (3.5 mmol) of $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$, 0.3 mL (0.26 g, 3.7 mmol) of $CH_3CH{=}CHO$, and 50 mL of toluene was boiled under reflux for 16 h in a flask covered with aluminum foil to exclude light. After removal of solvent in vacuum the residue was extracted with 100 mL of hexane. The concentrated extract was chromatographed on a 2 × 40 cm silica gel column. The major yellow band was eluted with 1:1 hexane–dichloromethane. Evaporation of the eluate followed by crystallization from a mixture of hexane and dichloromethane gave 1.27 g (59% yield) of yellow $[(i\text{-}Pr_2NP)_2OCHCH{=}CHMe]Fe_2(CO)_6$.

A similar procedure was used to prepare $[(i\text{-}Pr_2NP)_2OCMeCH{=}CHPh]Fe_2(CO)_6$ and $[(i\text{-}Pr_2NP)_2OCCH{=}CH(CH_2)_3]Fe_2(CO)_6$ from reactions of $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ with $PhCH{=}CHCOMe$ and 2-cyclohexenone, respectively.

Reaction of $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ with $(Me_2C{=}CH)_2CO$ (Phorone). A mixture of 6.2 g (11 mmol) of $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$, 1.9 mL (1.68 g, 12.2 mmol) of $(Me_2C{=}CH)_2CO$, and 150 mL of hexane was boiled under reflux for 80 h in a flask covered with aluminum foil to exclude light. After removal of volatile materials in vacuum the residue was extracted with ~100 mL of hexane. The hexane extract was concentrated and cooled to −10 °C to give 5.0 g (67% yield) of orange, air-stable crystalline $[(i\text{-}Pr_2NP)_2OC(CH{=}CMe_2)_2]Fe_2(CO)_6$.

---

(6) Gansow, O. A.; Burke, A. R.; Vernon, W. D. *J. Am. Chem. Soc.* **1972**, *94*, 2550.

(7) Wu, F.-J.; King, R. B. *Organomet. Synth.* **1988**, *4*, 152.

Table III. Proton-Decoupled Carbon-13 NMR Spectral Data (δ) for Compounds Derived from $(i\text{-Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$[a]

	isopropyl groups			
compd	CH	CH_3	terminal CO	other
$(i\text{-Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$[b]	53.6	22.6	212.2	P(CO)P; 202.2 (83)
$[(i\text{-Pr}_2\text{NP})_2\text{OCHPh}]\text{Fe}_2(\text{CO})_6$[c]	55.5, 54.8	23.9	213.5	Ph, 137.2, 128.6
$[(i\text{-Pr}_2\text{NP})_2\text{OCPh}_2]\text{Fe}_2(\text{CO})_6$[c]	57.7, 54.6	25.0, 23.8	212.9	CO, 87.8 dd (8, 6); Ph, 143.1, 143.0, 128.5, 128.3, 127.4
$[(i\text{-Pr}_2\text{NP})_2\text{OCHCH{=}CHMe}]\text{Fe}_2(\text{CO})_6$	54.7, 54.3	23.8, 23.5	213.2	CO, 79.0 t (9); =CH; 130.9 d (9), 127.4; Me, 18.0
$[(i\text{-Pr}_2\text{NP})_2\text{OCMeCH{=}CHPh}]\text{Fe}_2(\text{CO})_6$	56.8, 54.3	25.0, 23.6	213.4	CO, 83.5; Ph, 136.5, 129.5, 128.5, 126.3; CH, 131.3, 127.5; Me, 14.1
$[(i\text{-Pr}_2\text{NP})_2\text{OCCH{=}CH(CH}_2)_3]\text{Fe}_2(\text{CO})_6$	56.7, 54.2	24.8, 23.6	213.7, 213.4	CO, 80.7 dd (14, 8); CH, 134.2 d (7), 128.6 d (4); CH_2, 32.5, 26.9, 20.1 d (7)
$[(i\text{-Pr}_2\text{NP})_2\text{OC(CH{=}CMe}_2)_2]\text{Fe}_2(\text{CO})_6$	57.9, 54.2	25.2, 23.5	213.5	CO, 87.5; =C, 136.2 d (9); CH, 124.5; Me, 27.3, 19.4
$[(i\text{-Pr}_2\text{NP})_2\text{OCOCOCH{=}CH}]\text{Fe}_2(\text{CO})_6$	56.1, 54.9	24.3, 23.5	212.2	CO, 170.7, 154.5; CH, 123.8
$[(i\text{-Pr}_2\text{NP})_2\text{OCOCOC}_6\text{H}_4]\text{Fe}_2(\text{CO})_6$	56.7, 54.9	24.4, 24.0, 23.6	212.6, 210.6	CO, 168.5, 146.7 t (5); Ph, 134.7, 130.6, 128.2, 125.7, 123.3, 106 dd (17, 7)
$[(i\text{-Pr}_2\text{NP})_2\text{N{=}CMe}]\text{Fe}_2(\text{CO})_6$	54.5, 54.3	23.4, 23.1	212.7	CN, 196.2 dd (31, 7); Me, 22.2 t (33)
$[(i\text{-Pr}_2\text{NP})_2\text{N{=}CPh}]\text{Fe}_2(\text{CO})_6$	54.5, 54.3	23.0	213.0	CN, 194.4 dd (29, 10); Ph, 136.9 dd (35, 27), 129.6, 128.1, 126.0
$[(i\text{-Pr}_2\text{NP})_2\text{CH}_2\text{CHC}{\equiv}\text{N}]\text{Fe}_2(\text{CO})_6$	55.2, 54.5	24.3, 23.8	212.6, 212.1	CN, 120.8 d (10); CH_2, 37.9 dd (21, 3); CH, 33.2 dd (25, 6)
$[(i\text{-Pr}_2\text{NP})_2\text{NH{=}C{=}CHCO}_2\text{Et}]\text{Fe}_2(\text{CO})_6$	54.6, 54.2	23.9, 23.5	212.4	CN, 167.8; CO, 92.7; CH, 165.7 dd (27, 19); Et, 59.7, 14.3
$[(i\text{-Pr}_2\text{NPH})(\textit{nor}\text{-C}_7\text{H}_8\text{P})\text{Fe}_2(\text{CO})_6$	47.2	21	213.5, 213.2	*nor*-C_7H_8, 46.4 [2], 41.6 [1], 35.4 [1], 28.2 [1], 19.9 d (37) [2]

[a] CDCl_3 solutions. Abbreviations: d = doublet, t = triplet, dd = double doublet. Coupling constants in Hz are given in parentheses; relative intensities are given in brackets. [b] Data from: King, R. B.; Wu, F.-J.; Holt, E. M. *J. Am. Chem. Soc.* **1987**, *109*, 7764. [c] Data from: King, R. B.; Bhattacharyya, N. K.; Holt, E. M. *J. Organomet. Chem.* **1991**, *421*, 247.

Table IV. Proton NMR Spectral Data (δ) for Compounds Derived from $(i\text{-Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$[a]

	isopropyl groups		
compd	CH	CH_3	other
$(i\text{-Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$[b]	3.9–3.2	1.27 d (7)	
$[(i\text{-Pr}_2\text{NP})_2\text{OCHPh}]\text{Fe}_2(\text{CO})_6$[c]	3.92 sp (7), 2.54 sp (7)	1.35 d (7), 1.19 d (7), 0.92 d (7)	Ph, 7.40–7.26,[d] CH, 4.59 d (6)
$[(i\text{-Pr}_2\text{NP})_2\text{OCPh}_2]\text{Fe}_2(\text{CO})_6$[c]	3.97 sp (7), 3.57 sp (7)	1.39 d (7), 1.29 d (7)	Ph, 7.50 d (6), 7.26[d]
$[(i\text{-Pr}_2\text{NP})_2\text{OCHCH{=}CHMe}]\text{Fe}_2(\text{CO})_6$	3.87 sp (7), 3.71 sp (7)	1.33 d (7), 1.31 d (7)	=CH, 5.72–5.80,[d] 5.33–5.42,[d] CHO, 4.13 t (11); Me, 1.72–1.75[d]
$[(i\text{-Pr}_2\text{NP})_2\text{OCMeCH{=}CHPh}]\text{Fe}_2(\text{CO})_6$	3.93[d]	1.38	Ph, 7.34,[d] 7.26; =CH, 6.57 d (16), 6.32 d (16); Me, 1.73 d (11)
$[(i\text{-Pr}_2\text{NP})_2\text{OCCH{=}CH(CH}_2)_3]\text{Fe}_2(\text{CO})_6$	3.95 sp (7), 3.81 sp (7)	1.36 d (7), 1.31 d (7)	CH, 6.09–6.03,[d] 5.76–5.70,[d] CH_2, 1.75–2.23[d]
$[(i\text{-Pr}_2\text{NP})_2\text{OC(CH{=}CMe}_2)_2]\text{Fe}_2(\text{CO})_6$	3.98 sp (7), 3.81 sp (7)	1.33 d (7), 1.25 d (7)	=CH, 5.52;[d] Me, 1.67, 1.66
$[(i\text{-Pr}_2\text{NP})_2\text{OCOCOCH{=}CH}]\text{Fe}_2(\text{CO})_6$	3.81 sp (7)	1.28 dd (12, 6)	CH, 7.27 d (6), 6.21 d (6)
$[(i\text{-Pr}_2\text{NP})_2\text{OCOCOC}_6\text{H}_4]\text{Fe}_2(\text{CO})_6$	3.81 sp (7), 3.61 sp (7)	1.24 d (7) [2], 1.02 d (7) [1], 0.76 d (7) [1]	Ph, 7.83 d (8), 7.74 d (8), 7.66 t (7), 7.53 t (7)
$[(i\text{-Pr}_2\text{NP})_2\text{N{=}CMe}]\text{Fe}_2(\text{CO})_6$	3.57 sp (7)	1.23 dd (7, 5)	Me: 2.03 t (4)
$[(i\text{-Pr}_2\text{NP})_2\text{N{=}CPh}]\text{Fe}_2(\text{CO})_6$	3.73 sp (7), 3.48 sp (7)	1.31 d (6), 1.07 d (6)	Ph, 7.37, 7.26[d]
$[(i\text{-Pr}_2\text{NP})_2\text{CH}_2\text{CHC{=}N}]\text{Fe}_2(\text{CO})_6$	3.79 sp (7), 3.73 sp (7)	1.41 d (7) [1], 1.34 d (7) [1], 1.29 d (7) [1]	CH, 3.18–3.06;[d] CH_2, 2.42–2.29[d]
$[(i\text{-Pr}_2\text{NP})_2\text{NH{=}C{=}CHCO}_2\text{Et}]\text{Fe}_2(\text{CO})_6$	3.79 sp (7), 3.68 sp (7)	1.34 d (7), 1.30 d (7)	NH, 7.55 dd (43, 7); CH, 5.40 d (11); Et, 4.12 q (7), 1.27 t (7)
$(i\text{-Pr}_2\text{NPH})(\textit{nor}\text{-C}_7\text{H}_8\text{P})\text{Fe}_2(\text{CO})_6$	3.48 m	1.21 d (6), 1.19 d (6)	PH, 5.78 dd (380, 25); *nor*-C_7H_8, 2.76, 2.65 d (15), 2.36 d (1), 2.12, 1.96, 1.81, 1.56, 1.51

[a] The spectra were obtained in CDCl_3 solutions. Abbreviations: d = doublet, dd = double doublet, t = triplet, q = quartet, sp = septet; m = multiplet. Coupling constants in are given in parentheses; relative intensities are given in brackets. [b] Data from: King, R. B.; Wu, F.-J.; Holt, E. M. *J. Am. Chem. Soc.* **1987**, *109*, 7764. [c] Data from: King, R. B.; Bhattacharyya, N. K.; Holt, E. M. *J. Organomet. Chem.* **1991**, *421*, 247. [d] Not all of the resonances could be resolved.

Reaction of $(i\text{-Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ with Maleic Anhydide. A mixture of 3.4 g (6.0 mmol) of $(i\text{-Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$, 0.58 g (5.9 mmol) of maleic anhydride, and 100 mL of toluene was stirred for 16 h at 25 °C. The phosphorus-31 NMR spectrum of the reaction mixture showed only the δ 225 resonance of unchanged $(i\text{-Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$. The reaction mixture was therefore boiled under reflux for 10 h. After removal of volatile materials in vacuum, the residue was extracted with a mixture of 25 mL of hexane and 25 mL of dichloromethane. Concentrating and cooling the filtered exact to 10 °C gave 2.0 g (52% yield) of yellow, crystalline $[(i\text{-Pr}_2\text{NP})_2\text{OCOCOCH{=}CH}]\text{Fe}_2(\text{CO})_6$.

Reaction of $(i\text{-Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ with Phthalic Anhydride. A mixture of 4.1 g (7.2 mmol) of $(i\text{-Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$, 0.53 g (3.6 mmol) of phthalic anhydride, and 100 mL of toluene was boiled under reflux for 10 h. After removal of solvent the residue was chromatographed on silica gel using 1:1 hexane–dichloromethane to elute the major yellow band. After evaporation of the eluate the residue was washed with hexane and recrystallized from a mixture of hexane and dichloromethane to give 1.0 g (40% yield) of yellow $[(i\text{-Pr}_2\text{NP})_2\text{OCOCOC}_6\text{H}_4]\text{Fe}_2(\text{CO})_6$.

Reaction of $(i\text{-Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ with Acetonitrile. A solution of 4.9 g (8.6 mmol) of $(i\text{-Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ in 150 mL of acetonitrile was heated in an oil bath for 60 h at 100 °C. Acetonitrile was removed from the filtered reaction mixture at 25 °C/20 mm. A concentrated solution of the residue in a mixture of dichloromethane and hexane was chromatographed on a 2 × 40 cm silica gel column. The broad yellow-red band was eluted with 1:1 hexane–methylene chloride. Crystallization of the eluate gave 2.03 g (40% yield) of air-stable red $[(i\text{-Pr}_2\text{NP})_2\text{N{=}CMe}]\text{Fe}_2(\text{CO})_6$.

Reaction of $(i\text{-Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ with Benzonitrile. A solution of 2.0 g (3.5 mmol) of $(i\text{-Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ and 0.5 mL (0.50 g, 4.9 mmol) of benzonitrile in 50 mL of toluene was boiled under reflux for 10 h. A product isolation procedure similar to that given above for the

Table V. Crystal Data for $[(i\text{-}Pr_2NP)_2OCOCOCH{=}CH]Fe_2(CO)_6$, $[(i\text{-}Pr_2NP)_2N{=}CMe]Fe_2(CO)_6$, $[(i\text{-}Pr_2NP)_2CH_2CHC{\equiv}N]Fe_2(CO)_6$, $[(i\text{-}Pr_2NP)_2NH{=}C{=}CHCO_2Et]Fe_2(CO)_6$, and $[(i\text{-}Pr_2NPH)(nor\text{-}C_7H_8P)Fe_2(CO)_6$

	compound				
	$[(i\text{-}Pr_2NP)_2OCO\text{-}COCH{=}CH]Fe_2(CO)_6$	$[(i\text{-}Pr_2NP)_2N{=}CMe]\text{-}Fe_2(CO)_6$	$[(i\text{-}Pr_2NP)_2CH_2CHC{\equiv}N]\text{-}Fe_2(CO)_6$	$[(i\text{-}Pr_2NP)_2NH{=}C{=}CHCO_2Et]Fe_2(CO)_6$	$[(i\text{-}Pr_2NPH)(nor\text{-}C_7H_8P)\text{-}Fe_2(CO)_6$
mol wt	640.13	583.13	563.89	655.19	535.04
cryst dimens (mm)	0.175 × 0.225 × 0.450	0.50 × 0.25 × 0.33	0.250 × 0.375 × 0.450	0.18 × 0.13 × 0.42	0.20 × 0.18 × 0.50
cryst syst	triclinic	monoclinic	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/m$	$P\bar{1}$	Cc	$P\bar{1}$
a (Å)	9.679(6)	8.761(6)	8.783(2)	18.211(1)	7.783(7)
b (Å)	10.476(6)	14.362(6)	10.732(2)	10.762(2)	9.124(4)
c (Å)	15.440(3)	10.984(1)	15.753(2)	16.434(1)	17.635(8)
α (deg)	75.23(9)	90	70.99(2)	90	98.67(4)
β (deg)	73.73(6)	100.75(6)	77.00(2)	106.09	94.23(5)
γ (deg)	76.40(9)	90	85.47(2)	90	104.91(5)
V (Å^3)	1430.336	1357.776	1367.90	3094.77	1188.36
$F(000)$	660	604	554	1360	548
μ(Cu Kα) (cm^{-1})	96.8	100.7	100.06	89.5	114.4
D_{calcd} (g cm^{-1})	1.486	1.426	1.369	1.406	1.495
Z	2	2	2	4	2
no. of tot. reflcns	6013	3079	5995	3441	5086
no. of obsd reflcns	1540	1979	3333	2235	2444
octants collcd	+h,±k,±l	$+h,+k,\pm l$	$+h,\pm k,\pm l$	$+h,+k,\pm l$	$+h,\pm k,\pm l$
R	0.108	0.060	0.078	0.058	0.063
R_w	0.126	0.081	0.109	0.075	0.088

reaction of $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ with acetonitrile gave 0.47 g (21% yield) of deep red $[(i\text{-}Pr_2NP)_2N{=}CPh]Fe_2(CO)_6$.

Reaction of $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ with Acrylonitrile. A solution of 7.94 g (14 mmol) of $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ and 1.2 mL (0.97 g, 18.2 mmol) of acrylonitrile in 200 mL of toluene was boiled under reflux for 60 h. The phosphorus-31 NMR spectrum of the crude reaction mixture indicated the presence of a minor compound exhibiting doublets ($|J(P\text{–}P)| = 102$ Hz) centered at δ 212.2 and 209.0 in addition to the major product; the minor product could not be isolated in significant quantities. Removal of solvent and excess acrylonitrile from the filtered solution at reduced pressure followed by chromatography of the products on a silica gel column using 1:1 hexane–dichloromethane as the eluent gave 5.2 g (62% yield) of air-stable yellow crystalline $[(i\text{-}Pr_2NP)_2CH_2CHC{\equiv}N]Fe_2(CO)_6$.

Reaction of $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ with Ethyl Cyanoacetate. A suspension of 4.6 g (8.1 mmol) of $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ and 1.0 mL (1.06 g, 9.2 mmol) of 98% ethyl cyanoacetate in 300 mL of hexane was heated in an oil bath at 90 °C for 1 week. The progress of the reaction was monitored by disappearance of the 1720-cm^{-1} infrared frequency of the phosphorus-bridging carbonyl in the $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ starting material. Removal of solvent in vacuum from the filtered reaction mixture gave 3.1 g (58% yield) air-stable crystalline $[(i\text{-}Pr_2NP)_2NH{=}C{=}CHCO_2Et]Fe_2(CO)_6$.

Reaction of $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ with Norbornadiene. A solution of 2.51 g (4.4 mmol) of $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ and 0.6 mL (0.51 g, 5.6 mmol) of 99% norbornadiene in 140 mL of toluene was heated to 90–100 °C for 1 week. Solvent was removed in vacuum from the filtered reaction mixture. The residue was extracted with hexane, and the filtered hexane extract was evaporated in vacuum. The residue was dissolved in a minimum of a 1:1 mixture of dichloromethane and hexane. The solution was kept in a −10 °C freezer for 1 week. The resulting crystals were filtered out, washed with several portions of cold hexane, and dried in vacuum to give 0.57 g (24% yield) of yellow acicular $(i\text{-}Pr_2NPH)(nor\text{-}C_7H_8P)Fe_2(CO)_6$.

Reaction of $(CH_2)_3(CMe_2)_2NP)_2COFe_2(CO)_6$ with Norbornadiene. A solution of $(CH_2)_3(CMe_2)_2NP)_2COFe_2(CO)_6$[8] and excess norbornadiene in toluene was boiled under reflux for 1 week. The ^{31}P NMR spectrum of the resulting product showed only unchanged $[(CH_2)_3(CMe_2)_2NP]_2COFe_2(CO)_6$.

Determinations of the Structures of $[(i\text{-}Pr_2NP)_2OCOCOCH{=}CH]Fe_2(CO)_6$, $[(i\text{-}Pr_2NP)_2N{=}CMe]Fe_2(CO)_6$, $[(i\text{-}Pr_2NP)_2CH_2CHC{\equiv}N]Fe_2(CO)_6$, $[(i\text{-}Pr_2NP)_2NH{=}C{=}CHCO_2Et]Fe_2(CO)_6$, and $(i\text{-}Pr_2NPH)(nor\text{-}C_7H_8P)Fe_2(CO)_6$. Crystals of $[(i\text{-}Pr_2NP)_2OCOCOCH{=}CH]Fe_2(CO)_6$ (**IX**), $[(i\text{-}Pr_2NP)_2N{=}CMe]Fe_2(CO)_6$ (**VI**: R = Me), $[(i\text{-}Pr_2NP)_2CH_2CHC{\equiv}N]Fe_2(CO)_6$ (**VII**), $[(i\text{-}Pr_2NP)_2NH{=}C{=}CHCO_2Et]Fe_2(CO)_6$ (**VIII**), and $(i\text{-}Pr_2NPH)(nor\text{-}C_7H_8P)Fe_2(CO)_6$ (**XIII**) from hexane were fixed in a random orientation on a glass fiber and mounted on an Enraf-Nonius CAD-4 diffractometer equipped with a graphite crystal monochromator. Cell dimensions were determined by least-squares refinement of the angular positions of 25 independent reflections for each sample in the 15–25° θ range during the normal alignment procedure. Intensity data were collected over a θ range of 2–75° using the ω–2θ technique with a variable scan width and scan range using Cu Kα radiation (λ = 1.541 84 Å). A semiempirical absorption correction[9] was applied to each data set. Table V provides information relevant to the crystal cells and data collections.

The structural analyses were performed on a VAX 6210 using the MolEN structure analysis program system.[10] The structures were solved using SIR88 with 8 symbols.[11] All non-hydrogen atoms were located in several difference Fourier maps and then refined by full-matrix least-squares, first isotropically and then anisotropically. Hydrogens were not included in the analysis of the structures. The final unweighted R values were 0.108, 0.060, 0.078, 0.058, and 0.063 for $[(i\text{-}Pr_2NP)_2OCOCOCH{=}CH]Fe_2(CO)_6$ (**IX**), $[(i\text{-}Pr_2NP)_2N{=}CMe]Fe_2(CO)_6$ (**VI**: R = Me), $[(i\text{-}Pr_2NP)_2CH_2CHC{\equiv}N]Fe_2(CO)_6$ (**VII**), $[(i\text{-}Pr_2NP)_2NH{=}C{=}CHCO_2Et]Fe_2(CO)_6$ (**VIII**), and $(i\text{-}Pr_2NPH)(nor\text{-}C_7H_8P)Fe_2(CO)_6$ (**XIII**), respectively.

The structure determination of **VIII** was problematical; there was considerable uncertainty in the carbonyl group of the ester as illustrated by the large thermal ellipsoids in the ORTEP diagram. Several schemes were employed to treat the apparent disorder problem, but no scheme proved to be any better (as judged by agreement factors and geometric considerations) than normal anisotropic refinement of the atomic positions involved. There is a short approach (2.87(5) Å) between N20 and O25 which suggests hydrogen bonding between the ester carbonyl oxygen and the NH attached to P1 or, similarly, in the reversed enol form. The disorder is probably caused by the coexistence of both structures in the lattice. The refinement has produced an unusually long C–O ester bond (C26–O24 = 1.77(4) Å), as well as an unusually short C=O bond (C23–O25 = 1.15(4) Å) and C–O bond (C23–O24 = 1.19(3) Å). These anomalous bond lengths are likely due to the large thermal factors.

Structure **XIII** refined to a result which contained two abnormal bond lengths, C21–C22 = 1.74(2) Å, and, in the three-membered ring, C24–C26 = 1.38(2) Å. The entire nortricyclane unit was removed and relocated from a difference map and rerefined to the same result. No explanation of this behavior has been identified.

The structures of $[(i\text{-}Pr_2NP)_2OCOCOCH{=}CH]Fe_2(CO)_6$, $[(i\text{-}Pr_2NP)_2N{=}CMe]Fe_2(CO)_6$, $[(i\text{-}Pr_2NP)_2CH_2CHC{\equiv}N]Fe_2(CO)_6$, $[(i\text{-}Pr_2NP)_2NH{=}C{=}CHCO_2Et]Fe_2(CO)_6$, and $(i\text{-}Pr_2NPH)(nor\text{-}C_7H_8P)Fe_2(CO)_6$ are depicted in Figures 2–6, respectively. Bond distances and angles of $[(i\text{-}Pr_2NP)_2OCOCOCH{=}CH]Fe_2(CO)_6$, $[(i\text{-}Pr_2NP)_2N{=}CMe]Fe_2(CO)_6$, $[(i\text{-}Pr_2NP)_2CH_2CHC{\equiv}N]Fe_2(CO)_6$, $[(i\text{-}Pr_2\text{-}$

---

[8] King, R. B.; Wu, F.-J.; Holt, E. M. *J. Am. Chem. Soc.* **1987**, *109*, 7764.

[9] North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr.* **1968**, *A24*, 351.

[10] MolEN, An interactive Structure Solution Procedure, Enraf-Nonius, Delft, The Netherlands.

[11] Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, G.; Polidori, G.; Spagna, R.; Viterbo, D. *J. Appl. Crystallogr.* **1989**, *22*, 389.

NP)$_2$NH=C=CHCO$_2$Et]Fe$_2$(CO)$_6$, and (*i*-Pr$_2$NPH)(*nor*-C$_7$H$_8$P)Fe$_2$(CO)$_6$ are listed in Tables VI–XV.

Results and Discussion

Reactions of Organic Carbonyl Derivatives with (*i*-Pr$_2$NP)$_2$COFe$_2$(CO)$_6$. The previous paper of this series[1] reported reactions of (*i*-Pr$_2$NP)$_2$COFe$_2$(CO)$_6$ (I) with aldehydes and ketones to give products of the general type [(*i*-Pr$_2$NP)$_2$OCRR′]Fe$_2$(CO)$_6$ (V in Figure 1: R = R′ = H, Ph; R = Ph, R′ = H, Me; R + R′ = -(CH$_2$)$_5$-) in which the C=O double bond has added across the (*i*-Pr$_2$NP)$_2$Fe$_2$(CO)$_6$ unit formed by loss of the phosphorus-bridging carbonyl group in I. Reactions of (*i*-Pr$_2$NP)$_2$COFe$_2$(CO)$_6$ (I) with the olefinic aldehydes and ketones MeCH=CHO, PhCH=CHCOMe, 2-cyclohexenone, and (Me$_2$C=CH)$_2$CO all gave analogous products indicated by their spectroscopic properties (Tables II–IV) to have similar structures (V in Figure 1) in which the carbonyl group has added to the (*i*-Pr$_2$NP)$_2$Fe$_2$(CO)$_6$ unit without involvement of the carbon–carbon double bond. Thus the ^{31}P NMR chemical shifts of the NPFe$_2$O phosphorus atom and $|J(\mathrm{P–P})|$ coupling constants (Table II) were within 10 ppm and 12 Hz, respectively, of the values found for the structurally characterized benzaldehyde derivative[1] [(*i*-Pr$_2$NP)$_2$OCHPh]Fe$_2$(CO)$_6$ (V: R = Ph, R′ = H). The ^{31}P NMR chemical shifts of the NPFe$_2$C phosphorus atom in these products covered a wider range (δ 217–251) owing to the wider range of groups bonded to the NPFe$_2$C carbon atom. The ^{13}C resonance of the complexed carbonyl group exhibited a resonance in the range δ 79–88 similar to the range of δ 65–88 found for the reported[1] [(*i*-Pr$_2$NP)$_2$OCRR′]Fe$_2$(CO)$_6$ derivatives (V). The presence of intact olefinic carbon atoms in the products obtained from (*i*-Pr$_2$NP)$_2$COFe$_2$(CO)$_6$ (I) and the olefinic aldehydes and ketones MeCH=CHO, PhCH=CHCOMe, 2-cyclohexanone, and (Me$_2$C=CH)$_2$CO is indicated by ^{13}C resonances (Table III) in the olefinic range δ 124–137 in all four compounds as well as olefinic proton resonances (Table IV) in the range δ 5.3–6.6. In view of the unambiguous structural assignments by these spectroscopic methods, no structural determinations by X-ray diffraction were performed on any of these derivatives. These results indicate that, in unsaturated aldehydes and ketones, the carbon–oxygen double bond reacts in preference to the carbon–carbon double bond with the (*i*-Pr$_2$NP)$_2$Fe$_2$(CO)$_6$ unit.

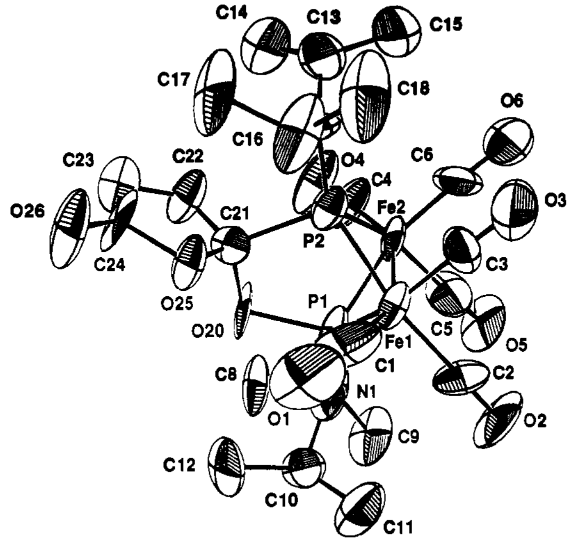
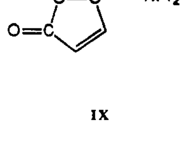


Figure 2. ORTEP diagram of [(*i*-Pr$_2$NP)$_2$OCOCOCH=CH]Fe$_2$(CO)$_6$ (IX).

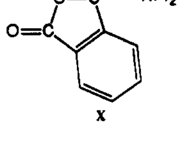
Table VI. Bond Distances (Å) in [(*i*-Pr$_2$NP)$_2$OCOCOCH=CH]Fe$_2$(CO)$_6$ (IX)

Fe1–Fe2	2.595(6)	O6–C6	1.10(3)
Fe1–P1	2.158(8)	O20–C21	1.43(3)
Fe1–P2	2.208(8)	O25–C21	1.45(2)
Fe1–C1	1.70(3)	O25–C24	1.46(3)
Fe1–C2	1.86(3)	O26–C24	1.30(4)
Fe1–C3	1.73(3)	N1–C7	1.51(3)
Fe2–P1	2.175(9)	N1–C10	1.43(3)
Fe2–P2	2.221(7)	N2–C13	1.42(3)
Fe2–C4	1.70(3)	N2–C16	1.53(3)
Fe2–C5	1.68(3)	C7–C8	1.56(3)
Fe2–C6	1.86(3)	C7–C9	1.60(3)
P1–O20	1.71(1)	C10–C11	1.56(4)
P1–N1	1.67(2)	C10–C12	1.61(3)
P2–N2	1.66(2)	C13–C14	1.54(4)
P2–C21	1.94(2)	C13–C15	1.46(4)
O1–C1	1.1793)	C16–C17	1.58(3)
O2–C2	1.10(3)	C16–C18	1.48(4)
O3–C3	1.22(3)	C21–H22	1.53(3)
O4–C4	1.18(3)	C22–C23	1.37(3)
O5–C5	1.22(3)	C23–C24	1.44(4)

The carbon–carbon double bond of maleic anhydride is very reactive generally undergoing reactions (e.g., the Diels–Alder reaction with 1,3-dienes) in preference to the anhydride carbonyl groups. For this reason maleic anhydride appeared to be a reasonable candidate for an organic substrate where a carbon–carbon double bond might react with the (*i*-Pr$_2$NP)$_2$Fe$_2$(CO)$_6$ unit from (*i*-Pr$_2$NP)$_2$COFe$_2$(CO)$_6$ (I) in preference to a carbon–oxygen bond. Reaction of maleic anhydride with (*i*-Pr$_2$NP)$_2$COFe$_2$(CO)$_6$ (I) in boiling toluene gave a product with the expected stoichiometry for a 1:1 maleic anhydride/(*i*-Pr$_2$NP)$_2$Fe$_2$(CO)$_6$ adduct. However, the carbon-13 NMR spectrum of this product (Table III) exhibited two different resonances assigned to organic carbonyl groups (δ 170.7 and 154.5). In addition, the proton NMR spectrum of this product (Table IV) exhibited a pair of coupled ($|J|$ = 6 Hz) olefinic proton doublets of δ 7.27 and 6.21. These NMR data suggest unsymmetrical bonding of maleic anhydride to the (*i*-Pr$_2$NP)$_2$Fe$_2$(CO)$_6$ unit as required by structure **IX** in which the (*i*-Pr$_2$NP)$_2$Fe$_2$(CO)$_6$ unit adds to one of the anhydride carbonyl groups of maleic anhydride leaving the other carbonyl group unaffected. Structure **IX** for the maleic anhydride adduct was confirmed by X-ray diffraction (Figure 2). In this structure the C21–O20 bond of the maleic anhydride carbonyl group bonded to the (*i*-Pr$_2$NP)$_2$Fe$_2$(CO)$_6$ unit is appreciably longer (1.43(3) Å) than the C24=O26 bond of the maleic anhydride carbonyl group not bonded to the (*i*-Pr$_2$NP)$_2$Fe$_2$(CO)$_6$ unit (1.30(4) Å) in accord with the reduction of C–O bond order from double to single upon addition of the (*i*-Pr$_2$NP)$_2$Fe$_2$(CO)$_6$ unit (Table VI). In this connection the 1.43(3) Å C21–O20 bond length is comparable to the single C–O bond lengths (1.46(3) Å for C24–O25 and 1.45(2) Å for C21–O25) in the maleic anhydride C$_4$O ring.



IX



X

The formation of **IX** by addition of (*i*-Pr$_2$NP)$_2$Fe$_2$(CO)$_6$ across one of the carbonyl groups of maleic anhydride without involvement of the carbon–carbon double bond suggested that a cyclic anhydride without an olefinic carbon–carbon double bond could form an analogous product. In this connection, the reaction of phthalic anhydride with (*i*-Pr$_2$NP)$_2$COFe$_2$(CO)$_6$ (I) led to a product [(*i*-Pr$_2$NP)$_2$OCOCOC$_6$H$_4$]Fe$_2$(CO)$_6$ formulated as **X** analogous to the maleic anhydride adduct **IX**. The unsymmetrical bonding of phthalic anhydride to the (*i*-Pr$_2$NP)$_2$Fe$_2$(CO)$_6$ unit in **X** is supported by the observation of a pair of organic carbonyl resonances at δ 168.5 and 146.7 similar to the pair of organic carbonyl resonances at δ 170.7 and 154.5 observed in **IX**. The assignment of the higher field of these two carbon resonances (i.e., the δ 154.5 resonance in **IX** and the δ 146.7 resonance in

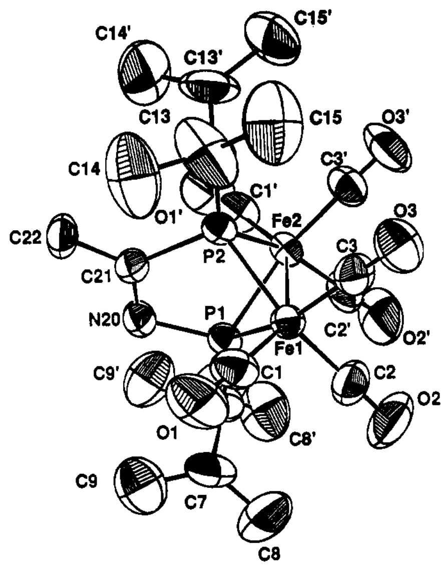


Figure 3. ORTEP diagram of $[(i\text{-}Pr_2NP)_2N{=}CMe]Fe_2(CO)_6$ (**VI**: R = Me, in Figure 1).

Table VII. Bond Angles (deg) in $[(i\text{-}Pr_2NP)_2\mathit{O}COCOCH{=}CH]Fe_2(CO)_6$ (**IX**)

Fe2–Fe1–P1	53.5(2)	C4–Fe2–C6	104.(2)	Fe1–C3–O3	177.(3)
Fe2–Fe1–P2	54.4(2)	C5–Fe2–C6	92.(1)	Fe2–C4–O4	177.(3)
Fe2–Fe1–C1	150.(1)	Fe1–P1–Fe2	73.6(3)	Fe2–C5–O5	174.(3)
Fe2–Fe1–C2	100.(1)	Fe1–P1–O20	112.0(6)	Fe2–C6–O6	176.(3)
Fe2–Fe1–C3	96.(1)	Fe1–P1–N1	132.2(8)	N1–C7–C8	111.(2)
P1–Fe2–P2	74.1(3)	Fe2–P1–O20	112.0(6)	N1–C7–C9	109.(2)
P1–Fe1–C1	105.(1)	Fe1–P1–N1	132.7(8)	C8–C7–C9	108.(2)
P1–Fe1–C2	92.(1)	Fe2–P1–O20	110.2(7)	N1–C10–C11	113.(3)
P1–Fe1–C3	149.(1)	Fe2–P1–N1	125.9(9)	N1–C10–C12	112.(2)
P2–Fe1–C1	102.(1)	O20–P1–N1	100.8(9)	C11–C10–C12	111.(2)
P2–Fe1–C2	154.(1)	Fe1–P2–Fe2	71.7(2)	N2–C13–C14	115.(3)
P2–Fe1–C3	91.(1)	Fe1–P2–N2	129.2(8)	N2–C13–C15	114.(3)
C1–Fe1–C2	102.(1)	Fe1–P2–C21	105.0(8)	C14–C13–C15	115.(3)
C1–Fe1–C3	104.(2)	Fe2–P2–N2	132.7(8)	N2–C16–C17	109.(2)
C2–Fe1–C3	92.(1)	Fe2–P2–C21	104.9(8)	N2–C16–C18	112.(3)
Fe1–Fe2–P1	52.9(2)	N2–P2–C21	107.(1)	C17–C16–C18	111.(3)
Fe1–Fe2–P2	53.9(2)	Fe2–P2–N2	132.7(8)	P2–C21–C20	106.(2)
Fe1–Fe2–C4	147.5(9)	Fe2–P2–C21	104.9(8)	P2–C21–O25	109.(2)
Fe1–Fe2–C5	99.(1)	P1–O20–C21	112.(1)	P2–C21–C20	116.(2)
Fe1–Fe2–C6	100.(1)	C21–O25–C24	102.(2)	O20–C21–O25	107.(2)
P1–Fe2–P2	73.5(3)	P1–N1–C7	114.(2)	O20–C21–C20	110.(2)
P1–Fe2–C4	104.(1)	P1–N1–C10	124.(2)	O25–C21–C20	109.(2)
P1–Fe2–C5	88.4(9)	C7–N1–C10	119.(2)	C21–C22–C23	108.(3)
P1–Fe2–C6	151.(1)	P2–N2–C13	127.(2)	C22–C23–C24	106.(3)
P2–Fe2–C4	101.0(8)	P2–N2–C16	113.(2)	O25–C24–O26	108.(3)
P2–Fe2–C5	154.(1)	C13–N2–C16	120.(2)	O25–C24–C23	115.(3)
P2–Fe2–C6	96.(1)	Fe1–C1–O1	177.(3)	O26–C24–C23	137.(3)
C4–Fe2–C5	101.(1)	Fe1–C2–O2	178.(3)		

X) to the anhydride carbonyl group adding across the $(i\text{-}Pr_2NP)_2Fe_2(CO)_6$ unit is supported by its appearance as a triplet ($|J|$ = 5 Hz) in **X** owing to coupling with the two phosphorus atoms of the $(i\text{-}Pr_2NP)_2Fe_2(CO)_6$ unit. This assignment of the higher field of the two carbonyl resonances in **IX** and **X** to the carbonyl group adding to the $(i\text{-}Pr_2NP)_2Fe_2(CO)_6$ unit is also consistent with the reduction of the carbon–oxygen bond order upon addition.

Reactions of Nitriles with $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$. Boiling an acetonitrile solution of $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ (**I**) led to a red product shown by X-ray diffraction (Figure 3) to be $[(i\text{-}Pr_2NP)_2N{=}CMe]Fe_2(CO)_6$ with structure **VI** (R = Me) in which the carbon–nitrogen triple bond of the acetonitrile has added across the $(i\text{-}Pr_2NP)_2Fe_2(CO)_6$ unit. The carbon–nitrogen triple bond distance of 1.16 Å in free acetonitrile[12] lengthens to 1.279(9) Å (Table VIII) upon addition to the $(i\text{-}Pr_2NP)_2Fe_2(CO)_6$ unit in accord with the reduction of the carbon–nitrogen bond order from three to two. The ^{13}C resonance (Table III) of the carbon in $[(i\text{-}Pr_2NP)_2N{=}CMe]Fe_2(CO)_6$ (**VI**: R = Me) appears at δ 196.2 as a double doublet ($|J_1|$ = 31 Hz, $|J_2|$ = 7 Hz) owing to nonequivalent coupling with the two phosphorus atoms. The considerable downfield chemical shift from the ^{13}C resonance in free acetonitrile (δ 117.7)[13] to that in $[(i\text{-}Pr_2NP)_2N{=}CMe]Fe_2(CO)_6$ (**VI**: R = Me) is also consistent with the reduction of bond order from three in free acetonitrile to two in **VI**. A particularly distinctive spectroscopic feature of $[(i\text{-}Pr_2NP)_2N{=}CR]Fe_2(CO)_6$ (**VI**: R = Me) is the very small phosphorus–phosphorus coupling constant $|J(P\text{–}P)|$ of 16 Hz in contrast to the $|J(P\text{–}P)|$ values of 102–138 Hz found for compounds obtained by addition of carbon–oxygen double bonds (e.g., those of aldehydes, ketones, and anhydrides) to the $(i\text{-}Pr_2NP)_2Fe_2(CO)_6$ unit (Table II).

Table VIII. Bond Distances (Å) in $[(i\text{-}Pr_2NP)_2C{=}NMe]Fe_2(CO)_6$ (**VI**: R = Me)

Fe1–Fe1′	2.593(2)	O2–C2	1.138(8)
Fe1–P1	2.214(2)	O3–C3	1.125(7)
Fe1–P2	2.242(2)	N1–C7	1.488(9)
Fe1–C1	1.774(7)	N2–C13	1.489(8)
Fe1–C2	1.770(7)	N20–C21	1.278(9)
Fe1–C3	1.804(6)	C7–C8	1.46(1)
P1–N1	1.650(6)	C7–C9	1.47(1)
P1–N20	1.742(7)	C13–C14	1.44(1)
P2–N2	1.649(6)	C13–C15	1.46(1)
P2–C21	1.893(8)	C21–C22	1.50(1)
O1–C1	1.143(7)		

Table IX. Bond Angles (deg) in $[(i\text{-}Pr_2NP)_2C{=}NMe]Fe_2(CO)_6$ (**VI**: R = Me)

Fe1–Fe1′–P1	54.15(3)	Fe1–P2–N2	127.4(2)
Fe1–Fe1′–P2	54.67(3)	Fe1–P2–C21	104.2(2)
Fe1–Fe1′–C1	146.9(2)	N2–P2–C21	114.4(3)
Fe1–Fe1′–C2	99.8(3)	P1–N1–C7	119.1(5)
Fe1–Fe1′–C3	100.3(2)	C7–N1–C7′	118.(1)
P1–Fe1–P2	72.72(6)	P2–N2–C13	120.7(4)
P1–Fe1–C1	100.7(2)	P1–N20–C21	111.7(5)
P1–Fe1–C2	93.0(2)	Fe1–C1–O1	179.0(6)
P1–Fe1–C3	154.5(2)	Fe1–C2–O2	178.6(7)
P2–Fe1–C1	100.4(2)	Fe1–C3–O3	177.3(6)
P2–Fe1–C2	154.5(3)	N1–C7–C8	115.8(8)
P2–Fe1–C3	93.8(2)	N1–C7–C9	117.4(8)
C1–Fe1–C2	103.1(3)	C8–C7–C9	125.9(9)
C1–Fe1–C3	103.0(3)	N2–C13–C14	117.4(8)
C2–Fe1–C3	90.6(3)	N2–C13–C15	117.1(8)
Fe1–P1–Fe1′	71.71(6)	C14–C13–C15	125.4(8)
Fe1–P1–N1	127.3(2)	P2–C21–N20	112.2(6)
Fe1–P1–N20	110.0(2)	P2–C21–C22	125.9(5)
N1–P1–N20	106.6(3)	N20–C21–C22	121.9(7)
Fe1–P2–Fe1	70.65(7)		

The carbon–nitrogen triple bond in benzonitrile was also found to add to the $(i\text{-}Pr_2NP)_2Fe_2(CO)_6$ unit to give a product $[(i\text{-}Pr_2NP)_2N{=}CPh]Fe_2(CO)_6$ formulated as **VI** (R = Ph) in view of the similarity of its spectroscopic properties to those of the acetonitrile adduct. Thus the benzonitrile derivative exhibited a $|J(P\text{–}P)|$ of 17 Hz like the acetonitrile complex and a double doublet ($|J_1|$ = 29 Hz, $|J_2|$ = 10 Hz) ^{13}C resonance at δ 194.4 from the carbon originating from the nitrile close to the δ 196.2 resonance for the corresponding carbon in the acetonitrile derivative.

The reaction of acrylonitrile with $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ (**I**) followed a different course. An adduct of similar stoichiometry was obtained. However, the spectroscopic properties of this complex were very different from those of the acetonitrile and benzonitrile complexes in the following ways: (1) The proton-decoupled ^{13}C resonance assigned to the nitrile carbon atom appeared at δ 120.8 indicative of an intact nitrile group; this resonance appeared as a doublet rather than a double doublet indicating appreciable coupling to only one of the two phosphorus

---

(12) Moffat, J. B. In *Supplement C: The Chemistry of Triple Bonded Functional Groups*; Patai, S., Rappoport, Z. Eds.; Wiley: Chichester, U.K., 1983; p 1019.

(13) Breitmaier, E.; Voelter, W. *^{13}C NMR Spectroscopy*, 2nd ed.; Verlag Chemie: Weinheim, Germany 1978; p 72.

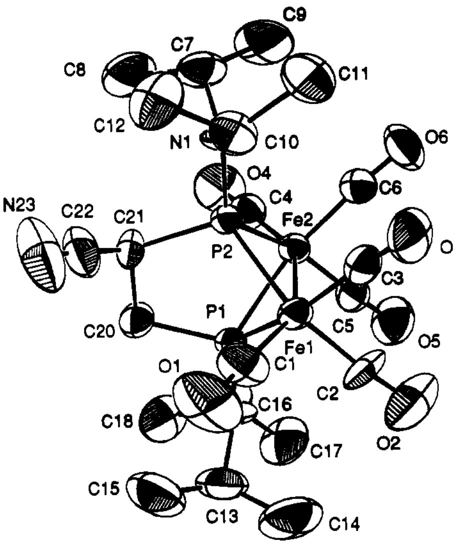


Figure 4. ORTEP diagram of $[(i\text{-}Pr_2NP)_2CH_2CHC{\equiv}N]Fe_2(CO)_6$ (VII in Figure 1).

Table X. Bond Distances (Å) in $[(i\text{-}Pr_2NP)_2CH_2CHC{\equiv}N]Fe_2(CO)_6$ (VII)

Fe1–Fe2	2.587(2)	O4–C4	1.15(1)
Fe1–P1	2.217(2)	O5–C5	1.17(1)
Fe1–P2	2.204(2)	O6–C6	1.16(1)
Fe1–C1	1.76(1)	N1–C7	1.49(1)
Fe1–C2	1.72(1)	N1–C10	1.50(1)
Fe1–C3	1.79(1)	N2–C13	1.49(1)
Fe2–P1	2.220(2)	N2–C16	1.54(2)
Fe2–P2	2.223(2)	N23–C22	1.14(1)
Fe2–C4	1.766(9)	C7–C8	1.54(1)
Fe2–C5	1.743(9)	C7–C9	1.53(2)
Fe2–C6	1.767(9)	C10–C11	1.56(1)
P1–N2	1.648(7)	C10–C12	1.55(2)
P1–C20	1.838(8)	C13–C14	1.56(2)
P2–N1	1.650(6)	C13–C15	1.48(2)
P2–C21	1.897(7)	C16–C17	1.53(1)
O1–C1	1.14(1)	C16–C18	1.51(2)
O2–C2	1.16(2)	C20–C21	1.53(1)
O3–C3	1.14(1)	C21–C22	1.46(1)

atoms. (2) The resonance assigned to the CH and CH_2 groups of the acrylonitrile by DEPT methods appeared in the high-field region (δ 37.9 for the CH_2 group and δ 33.2 for the CH group) associated with saturated carbon atoms rather than unsaturated carbon atoms. Thes spectroscopic observations suggested structure VII in which the carbon–carbon double bond rather than the carbon–nitrogen triple bond of the acrylonitrile had added to the $(i\text{-}Pr_2NP)_2Fe_2(CO)_6$ unit. This structure was confirmed by X-ray diffraction (Figure 4). The carbon–nitrogen bond length (Table X) of the isolated nitrile group in the acrylonitrile complex $[(i\text{-}Pr_2NP)_2CH_2CHC{\equiv}N]$ $Fe_2(CO)_6$ (VII) was only 1.14 Å consistent with the value for a free nitrile in contrast to the carbon–nitrogen bond length of 1.279 Å (Table VIII) for the carbon–nitrogen bond in $[(i\text{-}Pr_2NP)_2N{=}CMe]Fe_2(CO)_6$ (VI).

Table XI. Bond Angles (deg) in $[(i\text{-}Pr_2NP)_2CH_2CHC{\equiv}N]Fe_2(CO)_6$ (VII)

Fe2–Fe1–P1	54.39(6)	P2–Fe2–C4	102.3(3)	Fe1–C1–O1	178.2(8)
Fe2–Fe1–P2	54.60(6)	P2–Fe2–C5	155.7(3)	Fe1–C2–O2	174.8(8)
Fe2–Fe1–C1	149.0(3)	P2–Fe2–C6	90.2(3)	Fe1–C3–O3	176.4(8)
Fe2–Fe1–C2	92.7(3)	C4–Fe2–C5	100.5(4)	Fe2–C4–O4	179.6(9)
Fe1–Fe1–C3	104.8(3)	C4–Fe2–C6	104.5(4)	Fe2–C5–O5	176.4(8)
P1–Fe1–P2	74.50(8)	C5–Fe2–C6	92.1(4)	Fe2–C6–O6	176.2(8)
P1–Fe1–C1	100.0(3)	Fe1–P1–Fe2	71.32(7)	N1–C7–C8	114.0(8)
P1–Fe1–C2	90.6(3)	Fe1–P1–N2	127.3(3)	N1–C7–C9	113.(1)
P1–Fe1–C3	159.1(4)	Fe1–P1–C20	110.6(3)	C8–C7–C9	112.(1)
P2–Fe1–C1	105.7(3)	Fe2–P1–N2	125.3(3)	N1–C10–C11	108.7(9)
P2–Fe1–C2	147.0(3)	Fe2–P1–C20	109.8(3)	N1–C10–C12	111.8(9)
P2–Fe1–C3	95.2(3)	N2–P1–C20	108.0(4)	C11–C10–C12	110.2(9)
C1–Fe1–C2	105.8(4)	Fe1–P2–Fe2	71.49(7)	N2–C13–C14	112.(1)
C1–Fe1–C3	100.3(5)	Fe1–P2–N1	126.2(2)	N2–C13–C15	115.(1)
C2–Fe1–C3	88.7(4)	Fe1–P2–C21	109.9(3)	C14–C13–C15	114.(1)
Fe1–Fe2–P1	54.29(6)	Fe2–P2–N1	128.6(2)	N2–C16–C17	111.(1)
Fe1–Fe2–P2	53.91(6)	Fe2–P2–C21	106.9(3)	N2–C16–C18	111.(1)
Fe1–Fe2–C4	149.7(3)	N1–P2–C21	108.7(4)	C17–C16–C18	112.(1)
Fe1–Fe2–C5	101.8(3)	P2–N1–C7	124.6(7)	P1–C20–C21	107.9(5)
Fe1–Fe2–C6	94.9(3)	P2–N1–C10	119.3(6)	P2–C21–C20	107.9(5)
P1–Fe2–P2	74.07(8)	C7–N1–C10	115.8(8)	P2–C21–C22	110.3(6)
P1–Fe2–C4	104.8(3)	P1–N2–C13	124.9(8)	C20–C21–C22	111.3(8)
P1–Fe2–C5	92.2(3)	P1–N2–C16	116.8(6)	N23–C22–C21	179.(1)
P1–Fe2–C6	149.1(3)	C13–N2–C16	115.5(8)		

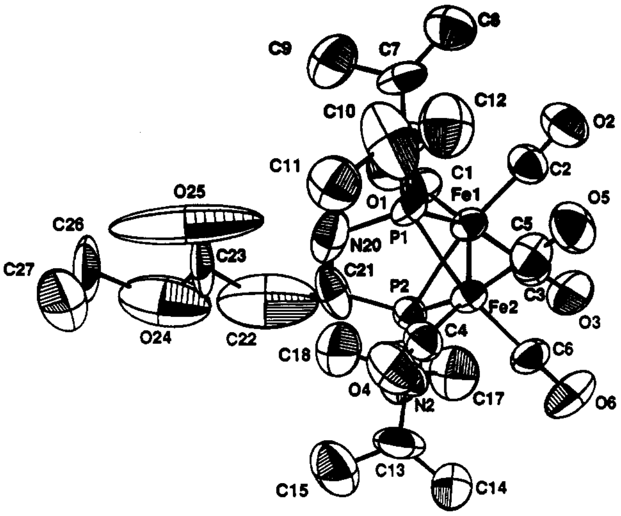
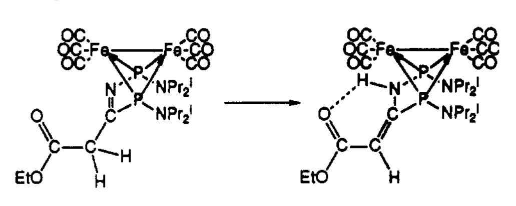


Figure 5. ORTEP diagram of $[(i\text{-}Pr_2NP)_2NH{=}C{=}CHCO_2Et](CO)_6$ (VIII).

The reaction of ethyl cyanoacetate, $N{\equiv}CCH_2CO_2Et$, with $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ was found to follow a still different course. The isolated product was a yellow air-stable solid shown by X-ray diffraction (Figure 5) to be $[(i\text{-}Pr_2NP)_2NHC{=}CHCO_2Et]Fe_2(CO)_6$ (VIII) formally derived by adding the tautomeric ketenimine form of ethyl cyanoacetate, namely $HN{=}C{=}CHCO_2Et$, across the $(i\text{-}Pr_2NP)_2Fe_2(CO)_6$ unit. The structure of VIII contains an N–H···O hydrogen bond from the ketenimine hydrogen to the ester carbonyl oxygen with an N2···O25 distance of 2.87(5) Å indicative of strong hydrogen bonding. The reaction of ethyl cyanoacetate with $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ could proceed by addition of the nitrile C≡N triple bond to the $(i\text{-}Pr_2NP)_2Fe_2(CO)_6$ unit to give $[(i\text{-}Pr_2NP)_2N{=}CCH_2CO_2Et]Fe_2(CO)_6$ (XI) similar to the formation of $[(i\text{-}Pr_2NP)_2N{=}CMe]Fe_2(CO)_6$ (VI) from acetonitrile and $(i\text{-}Pr_2NP)_2Fe_2(CO)_6$. Hydrogen transfer could then convert the complexed nitrile tautomer XI to be the complexed imine tautomer VIII as follows:



XI VIII

The C–N bond length in $[(i\text{-}Pr_2NP)_2NHC{=}CHCO_2Et]Fe_2(CO)_6$ (VIII) was found to be 1.43(2) Å (Table XII) in contrast to the C–N bond length in $[(i\text{-}Pr_2NP)_2N{=}CMe]Fe_2(CO)_6$ (VI) of 1.279(9) Å (Table VIII) in accord with the formal single C–N bond in VIII contrasted with the formal C=N double bond in VI. The C21–P2 bond length linking the original cyano carbon of the ethyl cyanoacetate to the $(i\text{-}Pr_2NP)_2Fe_2(CO)_6$ unit in VIII is abnormally short (1.68(2) Å) as contrasted with the corresponding C–P bond lengths of 1.84–1.94 Å in the other addition products of the $(i\text{-}Pr_2NP)_2Fe_2(CO)_6$ unit to C=X multiple bonds (Table XVI). This suggests considerable multiple bond character of the C21–P2 bond in accord with overlap of the filled π orbitals

Table XII. Bond Distances (Å) in $[(i\text{-Pr}_2\text{NP})_2\text{NH}{=}\text{C}{=}\text{CHCO}_2\text{Et}]\text{Fe}_2(\text{CO})_6$

Fe1–Fe2	2.592(2)	O6–C6	1.16(1)
Fe1–P1	2.175(3)	O24–C23	1.21(3)
Fe1–P2	2.232(3)	O24–C26	1.79(4)
Fe1–C1	1.83(1)	O25–C23	1.09(3)
Fe1–C2	1.76(1)	N1–C7	1.53(2)
Fe1–C3	1.83(1)	N1–C10	1.49(2)
Fe2–P1	2.214(3)	N2–C13	1.52(2)
Fe2–P2	2.265(3)	N2–C16	1.45(2)
Fe2–C4	1.74(1)	N20–C21	1.41(2)
Fe2–C5	1.74(1)	C7–C8	1.50(3)
Fe2–C6	1.82(1)	C7–C9	1.51(3)
P1–N1	1.63(1)	C10–C11	1.47(3)
P1–N20	1.75(2)	C10–C12	1.47(3)
P2–N2	1.65(1)	C13–C14	1.47(3)
P2–C21	1.68(2)	C13–C15	1.44(3)
O1–C1	1.10(2)	C16–C17	1.43(3)
O2–C2	1.13(1)	C16–C18	1.48(3)
O3–C3	1.13(2)	C21–C22	1.36(5)
O4–C4	1.16(2)	C22–C23	1.58(5)
O5–C5	1.14(2)	C26–C27	1.41(4)

Table XIII. Bond Angles (deg) in $[(i\text{-Pr}_2\text{NP})_2\text{NH}{=}\text{C}{=}\text{CHCO}_2\text{Et}]\text{Fe}_2(\text{CO})_6$

Fe2–Fe1–P1	54.50(9)	P2–Fe2–C6	90.6(4)	Fe1–C2–O2	177.(1)
Fe2–Fe1–P2	55.41(9)	C4–Fe2–C5	105.7(7)	Fe1–C3–O3	178.(1)
Fe2–Fe1–C1	147.5(4)	C4–Fe2–C6	101.7(6)	Fe2–C4–O4	176.(1)
Fe2–Fe1–C2	102.8(5)	C5–Fe2–C6	91.3(6)	Fe2–C5–O5	178.(1)
Fe2–Fe1–C3	97.2(5)	Fe1–P1–Fe2	72.4(1)	Fe2–C6–O6	176.(1)
P1–Fe1–P2	74.1(1)	Fe1–P1–N1	125.5(4)	N1–C7–C8	111.(2)
P1–Fe1–C1	102.8(4)	Fe1–P1–N20	107.3(6)	N1–C7–C9	113.(2)
P1–Fe1–C2	95.1(4)	Fe2–P1–N1	128.9(5)	C8–C7–C9	123.(2)
P1–Fe1–C3	151.7(5)	Fe2–P1–N20	107.1(6)	N1–C10–C11	119.(2)
P2–Fe1–C1	98.9(4)	N1–P1–N20	109.9(7)	N1–C10–C12	116.(2)
P2–Fe1–C2	158.2(5)	Fe1–P2–Fe2	70.4(1)	C11–C10–C12	119.(2)
P2–Fe1–C3	91.1(5)	Fe1–P2–N2	129.2(4)	N2–C13–C14	113.(2)
C1–Fe1–C2	102.0(6)	Fe1–P2–C21	107.6(7)	N2–C13–C15	120.(2)
C1–Fe1–C3	103.3(6)	Fe2–P2–N2	129.0(5)	C14–C13–C15	120.(2)
C2–Fe1–C3	90.0(6)	Fe2–P2–C21	106.6(6)	N2–C16–C17	118.(2)
Fe1–Fe2–P1	53.12(9)	N2–P2–C21	108.4(8)	N2–C16–C18	118.(2)
Fe1–Fe2–P2	54.21(8)	C23–O24–C26	104.(2)	C17–C16–C18	121.(2)
Fe1–Fe2–C4	148.2(5)	P1–N1–C7	115.(1)	P2–C21–N20	112.(1)
Fe1–Fe2–C5	97.6(5)	P1–N1–C10	121.(1)	P2–C21–C22	146.(2)
Fe1–Fe2–C6	99.0(4)	C7–N1–C10	123.(2)	N20–C21–C22	101.(2)
P1–Fe2–P2	72.7(1)	P2–N2–C13	119.(1)	C21–C22–C23	132.(2)
P1–Fe2–C4	103.4(5)	P2–N2–C16	123.(1)	O24–C23–O25	123.(3)
P1–Fe2–C5	93.4(5)	C13–N2–C16	117.(2)	O24–C23–C22	96.(3)
P1–Fe2–C6	152.1(4)	P1–N20–C21	110.(1)	O25–C23–C22	141.(3)
P2–Fe2–C4	151.6(5)	Fe1–C1–O1	177.(1)	O24–C26–C27	107.(2)
P2–Fe2–C5	101.6(5)				

Table XIV. Bond Distances (Å) in $(i\text{-Pr}_2\text{NPH})(nor\text{-C}_7\text{H}_8\text{P})\text{Fe}_2(\text{CO})_6$

Fe1–Fe2	2.674(2)	O5–C5	1.16(1)
Fe1–P1	2.183(2)	O6–C6	1.14(1)
Fe1–P2	2.210(2)	N1–C13	1.50(1)
Fe1–C1	1.76(1)	N1–C16	1.50(1)
Fe1–C2	1.773(9)	C13–C14	1.55(1)
Fe1–C3	1.78(1)	C13–C15	1.55(1)
Fe2–P1	2.180(3)	C16–C17	1.54(1)
Fe2–P2	2.202(2)	C16–C18	1.56(1)
Fe2–C4	1.77(1)	C21–C22	1.74(2)
Fe2–C5	1.77(1)	C21–C26	1.49(2)
Fe2–C6	1.78(1)	C22–C23	1.55(1)
P1–C21	1.83(1)	C22–C27	1.48(1)
P1–C23	1.859(9)	C23–C24	1.50(2)
P2–N1	1.625(6)	C24–C25	1.58(2)
O1–C1	1.14(1)	C24–C26	1.38(2)
O2–C2	1.16(1)	C25–C26	1.53(2)
O3–C3	1.14(1)	C25–C27	1.51(2)
O4–C4	1.12(1)		

of the adjacent C21═C22 double bond with the empty d orbitals of phosphorus P2. Note that the shortening of the C21–P2 bond to 1.68(2) Å in **VIII** is slightly less than the shortening of the P1–N1 and P2–N2 bonds in **VIII** to 1.63(1) and 1.65(1), respectively. These phosphorus–nitrogen bonds are assumed to have considerable multiple bond character arising from overlap of a nitrogen sp^2 hybrid orbital filled with its electron pair with an empty phosphorus d orbital.

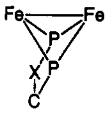
Table XV. Bond Angles (deg) in $(i\text{-Pr}_2\text{NPH})(nor\text{-C}_7\text{H}_8\text{P})\text{Fe}_2(\text{CO})_6$

Fe2–Fe1–P1	52.15(7)	P2–Fe2–C5	157.9(3)	N1–C13–C15	111.0(8)
Fe2–Fe1–P2	52.54(6)	P2–Fe2–C6	97.0(3)	C14–C13–C15	112.1(9)
Fe2–Fe1–C1	137.7(3)	C4–Fe2–C5	102.4(5)	N1–C16–C17	110.3(8)
Fe2–Fe1–C2	106.0(3)	C4–Fe2–C6	105.4(5)	N1–C16–C18	109.7(8)
Fe2–Fe1–C3	103.5(4)	C5–Fe2–C6	91.3(5)	C17–C16–C18	114.2(9)
P1–Fe1–P2	76.88(8)	Fe1–P1–Fe2	75.62(8)	P1–C21–C22	85.3(5)
P1–Fe1–C1	100.4(3)	Fe1–P1–C21	130.8(4)	P1–C21–C26	100.3(8)
P1–Fe1–C2	86.1(3)	Fe1–P1–C23	130.3(3)	C22–C21–C26	93.7(8)
P1–Fe1–C3	153.5(4)	Fe2–P1–C21	126.6(3)	C21–C22–C23	84.3(7)
P2–Fe1–C1	93.9(3)	Fe2–P1–C23	129.3(3)	C21–C22–C27	99.2(9)
P2–Fe1–C2	158.2(3)	C21–P1–C23	73.6(4)	C23–C22–C27	110.(1)
P1–Fe1–C3	96.7(3)	Fe1–P2–Fe2	74.63(8)	P1–C23–C22	89.8(6)
C1–Fe1–C2	102.7(4)	Fe1–P2–N1	128.8(3)	P1–C23–C24	101.9(8)
C1–Fe1–C3	105.7(5)	Fe2–P2–N1	128.8(3)	C22–C23–C24	98.8(8)
C2–Fe1–C3	92.4(4)	P2–N1–C13	120.0(5)	C23–C24–C25	110.(1)
Fe1–Fe2–P1	52.24(7)	P2–N1–C16	122.8(5)	C23–C24–C26	104.(1)
Fe1–Fe2–P2	52.83(6)	C13–N1–C16	117.2(6)	C25–C24–C26	61.7(9)
Fe1–Fe2–C4	138.9(4)	Fe1–C1–O1	176.5(9)	C24–C25–C26	52.5(7)
Fe1–Fe2–C5	105.4(3)	Fe1–C2–O2	175.5(9)	C24–C25–C27	105.(1)
Fe1–Fe2–C6	103.6(4)	Fe1–C3–O3	176.0(8)	C26–C25–C27	105.(1)
P1–Fe2–P2	77.12(8)	Fe2–C4–O4	179.(1)	C21–C26–C24	108.(1)
P1–Fe2–C4	100.7(4)	Fe2–C5–O5	176.(1)	C21–C26–C25	111.(1)
P1–Fe2–C5	86.4(3)	Fe2–C6–O6	176.(1)	C24–C26–C25	65.7(9)
P1–Fe2–C6	153.6(4)	N1–C13–C14	110.5(8)	C22–C27–C25	102.3(9)
P2–Fe2–C4	95.0(3)				

The proton NMR spectrum of $[(i\text{-Pr}_2\text{NP})_2\text{NHC}{=}\text{CHCO}_2\text{Et}]\text{Fe}_2(\text{CO})_6$ (**VIII**) (Table IV) exhibits a double doublet centered at δ 7.55 (J_1 = 43 Hz, J_2 = 7 Hz) which can be assigned to the imine N–H group in the ketenimine tautomer $[(i\text{-Pr}_2\text{NP})_2\text{NHC}{=}\text{CHCO}_2\text{Et}]\text{Fe}_2(\text{CO})_6$ (**VIII**) split differently by the two phosphorus atoms.

The isolation of **VIII** derived from the unusual ketenimine tautomer, HN═C═CHCO$_2$Et, of ethyl cyanoacetate from the reaction of $(i\text{-Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ with ethyl cyanoacetate suggests that complexation to a $(i\text{-Pr}_2\text{NP})_2\text{Fe}_2(\text{CO})_6$ unit can modify significantly the tautomeric equilibria in a multiply bonded carbon system. Complexation with $(i\text{-Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ units thus can be potentially useful for the stabilization of unusual tautomers.

Structural Features of CXP$_2$Fe$_2$ Cages. Additions of C═O, C≡N, and C═C multiple bonds to $(i\text{-Pr}_2\text{NP})_2\text{Fe}_2(\text{CO})_6$ units all lead to derivatives with six-atom CXP$_2$Fe$_2$ cages, which can be schematically represented as follows:



These cages have one Fe–Fe bond, four Fe–P bonds, one P–X bond, one P–C bond, and one C–X bond for a total of eight bonds. Similarly these cages have two P–Fe–P angles, four Fe–Fe–P angles, two Fe–P–Fe angles, two Fe–P–X angles, two Fe–P–C angles, one P–C–X angle, and one P–X–C angle for a total of 14 angles. Table XVI compares the dimensions of the CXFe$_2$P$_2$ cages in the four $[(i\text{-Pr}_2\text{NP})_2\text{CX}]\text{Fe}_2(\text{CO})_6$ derivatives structurally characterized in this paper as well as in the benzaldehyde derivative $[(i\text{-Pr}_2\text{NP})_2\text{OCHPh}]\text{Fe}_2(\text{CO})_6$ (**V**: R = Ph) reported previously. The C–X distances correlate with the C–X bond order since the 1.278(9) Å double bond C═N distance in $[(i\text{-Pr}_2\text{NP})_2\text{CNMe}]\text{Fe}_2(\text{CO})_6$ (**VI**: R = Me) is significantly shorter than the 1.43–1.53 Å single bond C–X distance in the other four $[(i\text{-Pr}_2\text{NP})_2\text{CX}]\text{Fe}_2(\text{CO})_6$ derivatives. The P–X distances correlate roughly with the electronegativity of the X atom with the shortest such distance being the 1.63 Å P–O distance in $[(i\text{-Pr}_2\text{NP})_2\text{OCHPh}]\text{Fe}_2(\text{CO})_6$ (**V**: R = H, R′ = Ph) and the longest such distance being the 1.897(7) Å P–C distance in $[(i\text{-Pr}_2\text{NP})_2\text{CH}_2\text{CHCN}]\text{Fe}_2(\text{CO})_6$ (**VII**: Table X). The dimensions of the Fe$_2$P$_2$ portions (Table XVI) of the CXFe$_2$P$_2$ cages appear to

Table XVI. Dimensions of the CXP_2Fe_2 Unit in (i-$Pr_2NP)_2CX]Fe_2(CO)_6$ Derivatives[a]

	bond distances (Å)					bond angles (deg)						
compd	C–X	P–X	P–C	Fe–Fe	Fe–P	P–C–X	P–X–C	Fe–P–X	Fe–P–C	P–Fe–P	Fe–Fe–P	Fe–P–Fe
$[(i\text{-}Pr_2NP)_2CNMe]Fe_2(CO)_6$	1.29	1.74	1.89	2.59	2.23	112.2	111.7	116.0	104.3	72.7	54.4	71.2
$[(i\text{-}Pr_2NP)_2NH{=}C{=}CHCO_2Et]Fe_2(CO)_6$	1.43	1.75	1.68	2.59	2.22	112	110	107.2	107.2	73.3	54.3	71.4
$[(i\text{-}Pr_2NP)_2OCHPh]Fe_2(CO)_6$[b]	1.44	1.63	1.92	2.60	2.22	103	115	111.1	96.8	72.5	*b*	72.0
$[(i\text{-}Pr_2NP)_2OCOCOCH{=}CH]Fe_2(CO)_6$	1.43	1.71	1.94	2.59	2.19	106	112	112	104.9	73.8	53.7	72.6
$[(i\text{-}Pr_2NP)_2CH_2CHCN]Fe_2(CO)_6$	1.53	1.90	1.84	2.59	2.22	107.9	107.9	108.4	110.2	74.3	54.3	72.7

[a] Distances are rounded to the nearest 0.01 Å, and angles, to the nearest 0.1°. In cases where there is more than one distance or angle of a given type (e.g., 4 Fe–P, 4 Fe–Fe–P, 2 Fe–P–Fe), the values are averaged. [b] Data reported in: King, R. B.; Bhattacharyya, N. K.; Holt, E. M. *J. Organomet. Chem.* **1991**, *421*, 247. The Fe–Fe–P angles were not obtained in this work.

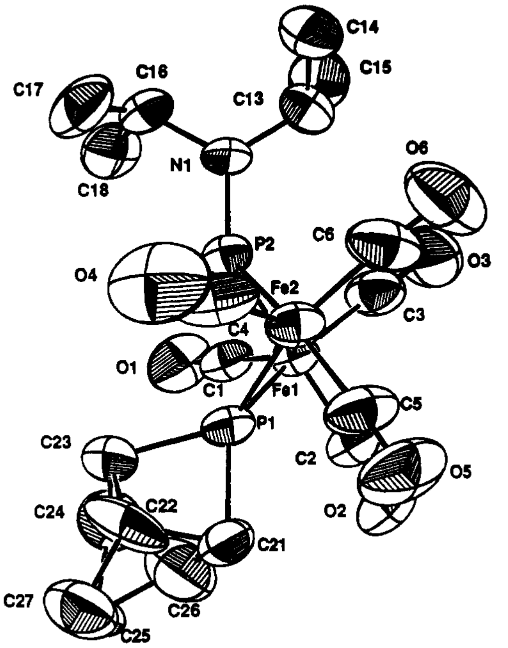


Figure 6. ORTEP diagram of (i-$Pr_2NPH)(nor$-$C_7H_8P)Fe_2(CO)_6$ (**XIII** in Figure 7).

be relatively insensitive to the nature of the C–X bonding. Thus in all five derivatives listed in Table XVI the Fe–Fe bond distances are 2.59 ± 0.01 Å, the Fe–P distances are 2.21 ± 0.02 Å, and the P–Fe–P, Fe–Fe–P, and Fe–P–Fe angles fall in the narrow ranges 73.3 ± 1, 54.0 ± 0.4, and 72.0 ± 0.8°, respectively.

Reaction of Norbornadiene with (i-$Pr_2NP)_2COFe_2(CO)_6$. The reaction of (i-$Pr_2NP)_2COFe_2(CO)_6$ with norbornadiene was also investigated during the course of this work with the hope of adding the (i-$Pr_2NP)_2Fe_2(CO)_6$ unit across the pair of norbornadiene double bonds to give the nortricyclane derivative **XII** (Figure 7). However, this reaction was found to follow a different course resulting in the loss of a diisopropylamino group to give a different type of nortricyclane derivative of stoichiometry (i-Pr_2NPH)(nor-$C_7H_8)Fe_2(CO)_6$ shown by X-ray diffraction (Figure 6) to have structure **XIII** (Figure 7).

The spectroscopic properties of (i-$Pr_2NPH)(nor$-$C_7H_8)Fe_2(CO)_6$ are consistent with the structure **XIII** found by X-ray diffraction. Thus the ^{31}P NMR spectrum of **XIII** (Table II) exhibits two doublets. The higher field doublet (δ 133.2) is split into an additional doublet ($|J|$ = 380 Hz) in the proton-coupled ^{31}P NMR spectrum indicating that this resonance arises from the i-Pr_2NPH group with the large coupling being $|^1J(P\text{–}H)|$; an essentially identical $|^1J(P\text{–}H)|$ of 381 Hz is found in a double doublet proton resonance centered at δ 5.78 (Table IV), which thus is assigned to the hydrogen directly bonded to phosphorus. The carbon-13 NMR spectrum of **XIII**, which has only a single diisopropylamino group, exhibits a single set of isopropyl CH and CH_3 resonances in contrast to all of the other new compounds prepared during the course of this work, which have two nonequivalent diisopropylamino groups (Table III).

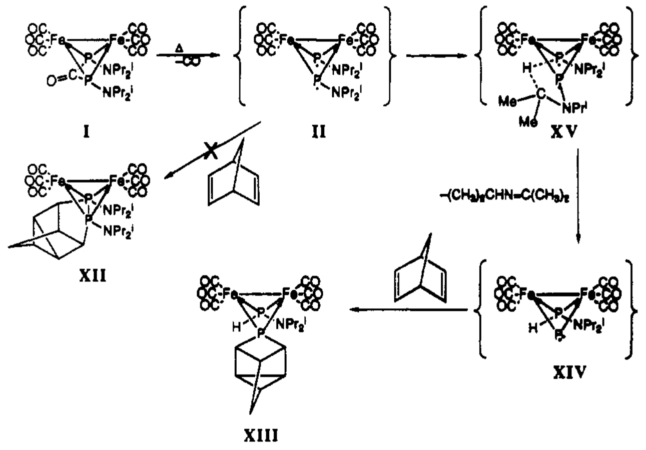
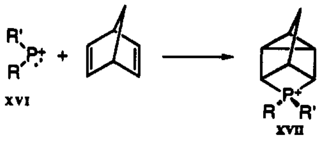


Figure 7. Proposed scheme for the reaction of norbornadiene with (i-$Pr_2NP)_2COFe_2(CO)_6$.

The structure **XIII** of (i-$Pr_2NPH)(nor$-$C_7H_8)Fe_2(CO)_6$ suggests the mechanism summarized in Figure 7 for the reaction of norbornadiene with (i-$Pr_2NP)_2COFe_2(CO)_6$ (**I**). In this mechanism the diradical **II** produced by pyrolytic phosphorus-bridging carbonyl extrusion from (i-$Pr_2NP)_2COFe_2(CO)_6$ (**I**) in the absence of a sufficiently reactive substrate is converted to the phosphinidene complex **XIV** with two-coordinate phosphorus by elimination of a $(CH_3)_2CHN{=}C(CH_3)_2$ unit from one of the diisopropylamino groups. This process can involve α-C–H activation of one of the diisopropylamino groups with transfer of that hydrogen to phosphorus (**XV** in Figure 7). A related process of isopropyl C–H activation (although a β-C–H rather than an α-C–H activation) on the (diisopropylamino)phosphenium ion $[i\text{-}Pr_2NPFe(CO)_2C_5Me_5]^+$ was reported by Gladysz and co-workers in 1984.[14] The formation of the nortricylane derivative **XIII** by addition of norbornadiene to the phosphinidene complex **XIV** is related to the reported[15] addition of norbornadiene to the two-coordinate phosphenium ions **XVI** to give the corresponding nortricyclane derivatives **XVII** according to the following general scheme:



The proposed scheme for the reaction of norbornadiene with the (i-$Pr_2NP)_2Fe_2(CO)_6$ unit (Figure 7) provides some insight as to why a stable tetrahedrane (i-$Pr_2NP)_2Fe_2(CO)_6$ (**III** in Figure 1) is not isolated when the phosphorus-bridging carbonyl (i-$Pr_2NP)_2COFe_2(CO)_6$ (**I**) is heated in the absence of a trapping agent. The structure of the reaction product obtained by heating norbornadiene with (i-$Pr_2NP)_2COFe_2(CO)_6$ (**I**) suggests that in the absence of a substrate an isopropyl α-C–H bond in the free

---

(14) Nakazawa, H.; Buhro, W. E.; Bertrand, G.; Gladysz, J. A. *Inorg. Chem.* **1984**, *23*, 3431.

(15) Weissman, S. A.; Baxter, S. C. *Tetrahedron Lett.* **1987**, *28*, 603.

diradical $(i\text{-}Pr_2NP)_2Fe_2(CO)_6$ (**II** in Figure 1) undergoes an addition reaction to the opposite phosphorus atom. The resulting product is unstable with the initial decomposition step resulting in elimination of $i\text{-}PrN{=}CMe_2$ leading to the complexed phosphinidene derivative **XIV**. Additional experimental evidence for the role of α-C–H bonds in a dialkylamino group providing a decomposition pathway for $(R_2NP)_2Fe_2(CO)_6$ tetrahedranes is provided by the observation that norbornadiene does not react in boiling toluene with the 2,2,6,6-tetramethylpiperidino derivative $(C_5H_6Me_4NP)_2COFe_2(CO)_6$, which has no α-C–H bonds for a reaction scheme similar to that depicted in Figure 7.

Summary

The results outlined in this paper indicate that the relative reactivity sequence of carbon multiple bonds toward the $(i\text{-}Pr_2NP)_2Fe_2(CO)_6$ unit is $C{=}O > C{=}C > C{\equiv}N$. The two experimental observations that clearly indicate this reactivity sequence are the following: (1) A C=O bond in maleic anhydride reacts with $(i\text{-}Pr_2NP)_2Fe_2(CO)_6$ in preference to the C=C bond. (2) The C=C bond in acrylonitrile reacts with $(i\text{-}Pr_2NP)_2Fe_2(CO)_6$ in preference to the C≡N bond. In addition the isolation of the complexed imine derivative $[(i\text{-}Pr_2NP)_2NHC{=}CHCO_2Et]Fe_2(CO)_6$ (**VIII**) from the reaction of ethyl cyanoacetate with $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ suggests that complexation with a $(i\text{-}Pr_2NP)_2Fe_2(CO)_6$ unit can be used to modify tautomeric equilibria in organic systems. This result may also suggest that C=N bonds in imines might react with $(i\text{-}Pr_2NP)_2Fe_2(CO)_6$ more readily than the C≡N bonds in nitriles.

Supplementary Material Available: Tables of positional parameters, anisotropic displacement parameters, and bond distances and angles (32 pages). Ordering information is given on any current masthead page.