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Dialkylamino Phosphorus Metal Carbonyls. 9. Acylation Rather Than Wittig Olefination in Reactions of the Phosphorus-Bridging Carbonyl Derivative $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ with Phosphonium Methylides[1]

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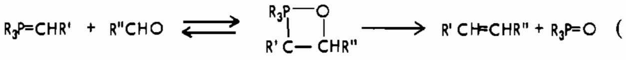
Reactions of the phosphorus-bridging carbonyl derivative $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ with the phosphonium methylides $R_3P{=}CH_2$ (R = Me, Me_2N, Ph, *p*-tolyl) in diethyl ether at room temperature do not result in the formation of the corresponding olefin $[(i\text{-}Pr_2NP)_2C{=}CH_2]Fe_2(CO)_6$ in a typical Wittig olefination reaction. Instead, the stable 1:1 adducts $[(i\text{-}Pr_2NP)_2HCOCHPR_3]Fe_2(CO)_6$ are formed. X-ray diffraction on $[(i\text{-}Pr_2NP)_2HCOCHP(C_6H_4Me\text{-}p)_3]Fe_2(CO)_6$ (monoclinic, space group $P2_1$; $a = 10.925$ (6) Å, $b = 14.822$ (4) Å, $c = 14.581$ (6) Å, $\beta = 109.05$ (3)°, $Z = 2$) indicates that the phosphorus-bridging carbonyl group has acylated the ylide carbon atom in $R_3P{=}CH_2$ to give a new type of phosphonium acylmethylide.

Introduction

One of the most generally useful methods for the synthesis of olefins is the Wittig olefination[2] of an aldehyde or ketone with a phosphonium ylide through a 1,2-oxaphosphetane intermediate, as exemplified by the following reaction:



$$R_3P{=}CHR' + R''CHO \rightleftharpoons \begin{matrix} R_3P - O \\ | \quad\;\; | \\ R'C - CHR'' \end{matrix} \longrightarrow R'CH{=}CHR'' + R_3P{=}O \quad (1)$$

We attempted to extend this type of Wittig olefination reaction to the readily available[3,4] air-stable phosphorus-bridging carbonyl derivative $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ (I in Figure 1) using the phosphonium methylides $R_3P{=}CH_2$ (R = Me, Me_2N, Ph, *p*-tolyl). These reactions were found to yield easily the 1:1 adducts $[(i\text{-}Pr_2NP)_2HCOCHPR_3]Fe_2(CO)_6$. However, these adducts did not eliminate phosphine oxide to give the corresponding olefin $[(i\text{-}Pr_2NP)_2C{=}CH_2]Fe_2(CO)_6$ (III in Figure 1) in the usual manner of the Wittig olefination reaction (eq 1). The reason for this anomalous chemical reactivity of these adducts was indicated by the structure of the tri-*p*-tolylphosphorus derivative $[(i\text{-}Pr_2NP)_2HCOCHPpTo_3]Fe_2(CO)_6$ (pTo = *p*-tolyl), which was shown by X-ray diffraction to be a novel "stabilized" phosphonium acylmethylide (IV in Figure 1) formed by an unexpected hydrogen migration from carbon to phosphorus. Details of this work are presented in this paper.

Experimental Section

Microanalyses were performed by the Atlantic Microanalytical Laboratory, Atlanta, GA. Infrared spectra (Table I) were run in the 2200–1400-cm^{-1} region, by using CH_2Cl_2 solutions and a Digilab FTS-60 Fourier transform infrared spectrometer. Phosphorus-31 (Table II), proton (Table III), and carbon-13 (Table IV) NMR spectra were taken on a JEOL FX-90Q (^{31}P and ^{13}C) or JEOL FX 270 (proton) spectrometer using $CDCl_3$ solutions and internal Me_4Si or external 85% phosphoric acid as references. 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*-Pr_2NH through $Na_2Fe(CO)_4{\cdot}1.5C_4H_8O_2$ and *i*-Pr_2NPCl_2 by using the published procedure.[4,5] The phosphonium ylides were prepared from commercial $Ph_3PMe^+Br^-$, $Me_4P^+I^-$, pTo_3P, $(Me_2N)_3P$, and *n*-butyllithium by using published procedures,[6,7] except for the substitution of *n*-BuLi for $NaNH_2$ in the preparation of $(Me_2N)_3P{=}CH_2$. Procedures for solvent purification and inert atmosphere handling are similar to those described in earlier papers.[4]

Reaction of $Ph_3P{=}CH_2$ with $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$. A yellow solution of $Ph_3P{=}CH_2$ obtained from 4.0 g (11.2 mmol) of $Ph_3PMe^+Br^-$ and 8.8 mL of 1.6 M *n*-BuLi in hexane (14.0 mmol) in 250 mL of diethyl ether at 0 °C was treated at 0 °C with a solution of 6.4 g (11.2 mmol) of $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ in 50 mL of diethyl ether. After several days of stirring at room temperature, the solvent was removed in vacuo. Crystallization of the residue from a mixture of tetrahydrofuran and hexane gave a yellow-brown solid lithium bromide adduct of approximate stoichiometry $[(i\text{-}Pr_2NP)_2HCOCHPPh_3]Fe_2(CO)_6{\cdot}LiBr$. Anal. Calcd for $C_{38}H_{45}BrFe_2LiN_2O_7P_3$: C, 48.9; H, 4.8; Br, 8.6; N, 3.0. Found on two independent preparations: C, 49.6, 49.3; H, 5.6, 5.8; Br, 8.4, 8.3; N, 2.8, 2.7.

In order to remove the coordinated lithium bromide, a concentrated tetrahydrofuran solution of the crude product was passed through a silica gel column. The eluate was evaporated in vacuo and the residue was washed with hexane to give 2.8 g (27% yield) of yellow $[(i\text{-}Pr_2NP)_2HCOCHPPh_3]Fe_2(CO)_6$, mp 148 °C dec. Anal. Calcd for $C_{38}H_{45}Fe_2N_2O_7P_3$: C, 53.9; H, 5.4; N, 3.3; Br, 0.0. Found: C, 53.5; H, 5.4; N, 3.3; Br, 0.0.

Reaction of $pTo_3P{=}CH_2$ with $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$. Commercial pTo_3P was converted to $pTo_3PMe^+I^-$ by reaction with methyl iodide in diethyl ether at room temperature. A yellow solution of $pTo_3P{=}CH_2$ from 2.6 g (5.8 mmol) of $pTo_3PMe^+I^-$ and 5.9 mmol of *n*-BuLi in 200 mL of diethyl ether was stirred overnight at room temperature with 3.4 g (5.9 mmol) of $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$. A workup procedure similar to that given above for $[(i\text{-}Pr_2NP)_2HCOCHPPh_3]Fe_2(CO)_6$ including chromatography of a tetrahydrofuran solution in silica gel gave 1.64 g (31% yield) of yellow $[(i\text{-}Pr_2NP)_2HCOCHPpTo_3]Fe_2(CO)_6$, mp 152 °C dec. Anal. Calcd for $C_{41}H_{51}Fe_2N_2O_7P_3$: C, 55.4; H, 5.8; N, 3.1. Found: C, 54.8; H, 5.9; N, 3.1.

Heating $[(i\text{-}Pr_2NP)_2HCOCHPpTo_3]Fe_2(CO)_6$ overnight in boiling toluene led to decomposition with no phosphorus-31 NMR evidence for the formation of the olefin $[(i\text{-}Pr_2NP)_2C{=}CH_2]Fe_2(CO)_6$.

Reaction of $Me_3P{=}CH_2$ with $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$. A solution of $Me_3P{=}CH_2$ obtained from 2.2 g (10 mmol) of $Me_4P^+I^-$ and 7.2 mL of 1.4 M MeLi in 300 mL of diethyl ether was stirred for 3 days at room temperature with 5.7 g (10 mmol) of $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$. A workup procedure similar to that given above for $[(i\text{-}Pr_2NP)_2HCOCHPPh_3]Fe_2(CO)_6$ including chromatography on silica gel gave 0.5 g (8% yield) of yellow $[(i\text{-}Pr_2NP)_2HCOCHPMe_3]Fe_2(CO)_6$, mp 170 °C dec. Anal. Calcd for $C_{23}H_{39}Fe_2N_2P_3O_7$: C, 41.8; H, 6.0; N, 4.2. Found: C, 40.7; H, 5.9; N, 4.1.

Reaction of $(Me_2N)_3P{=}CH_2$ with $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$. Commercial $(Me_2N)_3P$ was converted to $(Me_2N)_3PMe^+I^-$ by reaction with methyl iodide at −78 °C followed by warming to room temperature. Treatment of 6.7 g (22 mmol) of $(Me_2N)_3PMe^+I^-$ in 150 mL of diethyl ether at −78 °C with 15 mL of 1.6 M *n*-BuLi in hexane (24 mmol) followed by stirring overnight at room temperature gave 1.9 g (50% yield) of air-sensitive liquid $(Me_2N)_3P{=}CH_2$, bp 68 °C/0.3 mm (lit.[7] bp 87–88 °C/14 mm) after filtration, solvent removal, and vacuum distillation. A solution of 5.7 g (10 mmol) of $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ in 200 mL of diethyl ether was treated at −78 °C with 1.8 g (10 mmol) of vacuum distilled $(Me_2N)_3P{=}CH_2$. After overnight stirring at room temperature, solvent was removed from the reaction mixture under a vacuum. Crystallization of the residue from a mixture of diethyl ether and hexane gave 1.9 g (26% yield) of yellow-orange $[(i\text{-}Pr_2NP)_2HCOCHP(NMe_2)_3]Fe_2$-

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(1) For part 8 of this series see: King, R. B.; Bhattacharyya, N. K.; Holt, E. M. *J. Organomet. Chem.* **1990**, *394*, 305.

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Table I. Infrared ν(CO) Frequencies of $[(i\text{-Pr}_2NP)_2HCOCHPR_3]Fe_2(CO)_6$ and Related Compounds[a]

compd[b]	metal ν(CO), cm^{-1}	ν(CO) of $R_3P{=}CC({=}O)P$, cm^{-1}
$[(i\text{-Pr}_2NP)_2HCOCHPMe_3]Fe_2(CO)_6$	2037 s, 1998 s, 1970 s, 1946 s	1422 s
$[(i\text{-Pr}_2NP)_2HCOCHP(NMe_2)_3]Fe_2(CO)_6$	2036 s, 1996 s, 1971 s, 1944 s	1422 s
$[(i\text{-Pr}_2NP)_2HCOCHPPh_3]Fe_2(CO)_6$	2038 s, 1998 s, 1971 s, 1947 s	1422 s
$[(i\text{-Pr}_2NP)_2HCOCHPpTo_3]Fe_2(CO)_6$	2037 s, 1998 s, 1967 s, 1947 s	1422 s

[a] All of these spectra were obtained in CH_2Cl_2 solution. [b] The following abbreviations are used in these tables and elsewhere in the paper; Me = methyl, *i*-Pr = isopropyl, Ph = phenyl, pTo = *p*-tolyl.

Table II. Phosphorus-31 NMR Spectra of $[(i\text{-Pr}_2NP)_2HCOCHPR_3]Fe_2(CO)_6$ Derivatives

	phosphorus-31 NMR,[a] δ			
compd	$i\text{-Pr}_2NPCFe_2$	$i\text{-Pr}_2NPHFe_2$	^1J(P–H), Hz	R_3P
$[(i\text{-Pr}_2NP)_2HCOCHPMe_3]Fe_2(CO)_6$	224.1 dd (117, 44)	151.1 d (117)	408	7.5 d (44)
$[(i\text{-Pr}_2NP)_2HCOCHP(NMe_2)_3]Fe_2(CO)_6$	227.6 dd (110, 66)	151.6 d (110)	408	61.2 d (66)
$[(i\text{-Pr}_2NP)_2HCOCHPPh_3]Fe_2(CO)_6$				
isolated product	218.5 dd (117, 51)	148.6 d (117)	408	14.4 d (51)
minor product[b]	*c*	161.0 d (66)	*d*	16.9 d (51)
$[(i\text{-Pr}_2NP)_2HCOCHPpTo_3]Fe_2(CO)_6$				
isolated product	219.5 dd (117, 51)	149.3 d (117)	402	13.2 d (51)
minor product[e]	*c*	162.0 d (66)	*d*	13.6 d (59)

[a] Abbreviations: d = doublet, dd = double doublet. Coupling constants in Hz are given in parentheses. [b] Detected in the crude reaction mixture when run in tetrahydrofuran but not in diethyl ether. [c] Hidden under corresponding resonance of the major product. [d] Not determined. [e] Detected in the crude reaction mixture.

Table III. Proton NMR Spectra of $[(i\text{-Pr}_2NP)_2HCOCHPR_3]Fe_2(CO)_6$ Derivatives

	proton NMR,[a] δ				
compd	P–H	R_3PCH	CH(*i*-Pr)	CH_3(*i*-Pr)	R
$[(i\text{-Pr}_2NP)_2HCOCHPMe_3]Fe_2(CO)_6$	5.90 dd (406, 22)	3.81 d (27)	3.71 m 3.52 m	1.23 d (7) 1.19 d (7)	Me: 1.65 d (14)
$[(i\text{-Pr}_2NP)_2HCOCHP(NMe_2)_3]Fe_2(CO)_6$	5.84 dd (406, 22)	3.94 d (22)	3.72 m 3.52 m	1.25 d (7) 1.19 d (6)	Me_2N: 2.62 d (11)
$[(i\text{-Pr}_2NP)_2HCOCHPPh_3]Fe_2(CO)_6$	5.88 dd (406, 23)	4.34 d (25)	3.69 m 3.53 m	1.19 d (7) 1.15 d (7)	Ph: 7.64 dd (12, 7), 7.53 dd (9, 7), 7.44 dd (7, 3)
$[(i\text{-Pr}_2NP)_2HCOCHPpTo_3]Fe_2(CO)_6$	5.85 dd (406, 22)	4.28 d (25)	3.71 m 3.52 m	1.19 d (6) 1.16 d (8)	C_6H_4: 7.49 dd (13, 8), 7.21 t (7) Me: 2.36

[a] Abbreviations: d = doublet, dd = double doublet, t = triplet, m = multiplet. Coupling constants in Hz, are given in parentheses.

Table IV. Proton-Decoupled Carbon-13 NMR Spectra of $[(i\text{-Pr}_2NP)_2HCOCHPR_3]Fe_2(CO)_6$ Derivatives

	carbon-13 NMR,[a] δ					
compd	MCO	PCO	R_3PCH	CH(*i*-Pr)	CH_3(*i*-Pr)	R
$[(i\text{-Pr}_2NP)_2HCOCHPMe_3]Fe_2(CO)_6$	214.6	190.4[b]	*c*	54.7 48.5	23.6 22.0	Me: 11.9 d (41)
$[(i\text{-Pr}_2NP)_2HCOCHP(NMe_2)_3]Fe_2(CO)_6$	214.8	188.5 d (12)	61.8 t (76)	54.7 48.4	23.8 22.0	Me_2N: 36.9 d (4)
$[(i\text{-Pr}_2NP)_2HCOCHPPh_3]Fe_2(CO)_6$	214.6	189.1 d (25)	*c*	54.7 48.5	23.6 22.0	Ph: 133.1 d (10), 132.2, 128.8 d (14), 125.8 d (90)
$[(i\text{-Pr}_2NP)_2HCOCHPpTo_3]Fe_2(CO)_6$	214.6	189.3 d (12)	65.0 d (138)	54.6 48.4	23.6 22.0	C_6H_4: 142.6, 133.0 d (10), 129.5 d (14), 122.9 d (92) Me: 21.5

[a] The resonances indicated by d were doublets with coupling constants in Hz indicated in parentheses; the other resonances appeared as singlets under the conditions of proton decoupling. [b] The signal-to-noise ratio was too low to observe the splitting of this resonance. [c] These resonances are expected to be weak and were not unequivocally observed.

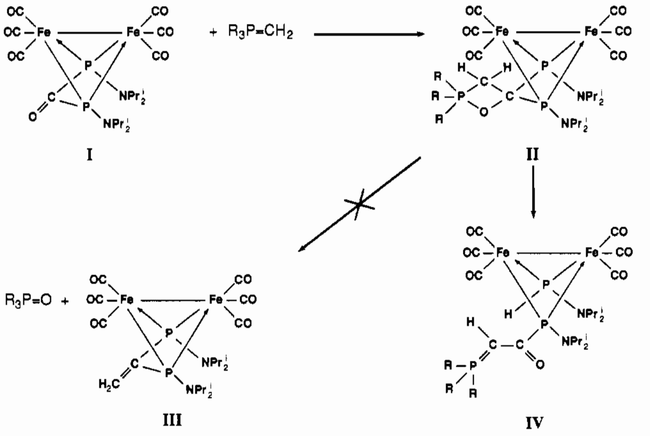

Figure 1. Possible scheme for the reactions of $(i\text{-Pr}_2NP)_2COFe_2(CO)_6$ with the phosphonium methylides $R_3P{=}CH_2$ (R = Me, Me_2N, Ph, pTo).

Table V. Crystallographic and Data Collection Parameters for $[(i\text{-Pr}_2NP)_2HCOCHPpTo_3]Fe_2(CO)_6$

formula	$C_{41}H_{51}N_2P_3Fe_2O_7$	μ(Mo Kα)	8.00 cm^{-1}
MW	888.5	λ (Mo Kα)	0.71069 Å
a	10.925 (6) Å	D_{calc}	1.322 g cm^{-3}
b	14.822 (4) Å	*Z*	2
c	14.581 (6) Å	space group	$P2_1$
α	90.0°	no. obs reflns	2648
β	109.05 (3)°	octants measd	$\pm h,k,l$
γ	90.0°	R/R_w	5.8/7.2%
V	2231.9 (14) $Å^3$	GOF	0.29
F(000)	1856		

$(CO)_6$, mp 112 °C dec. The analytical sample was purified further by chromatography on silica gel. Anal. Calcd for $C_{26}H_{48}Fe_2N_5O_7P_3$: C, 41.8; H, 6.5; N, 9.4. Found: C, 41.7; H, 6.4; N, 9.4.

X-ray Structure Determination of $[(i\text{-Pr}_2NP)_2HCOCHPpTo_3]Fe_2(CO)_6$. A single crystal of $[(i\text{-Pr}_2NP)_2HCOCHPpTo_3]Fe_2(CO)_6$ from diethyl ether was mounted on a Syntex P3 automated diffractometer. Unit cell dimensions (Table V) were determined by least-squares re-

Table VI. Positional Parameters for $C_{41}H_{51}N_2P_3Fe_2O_7$

atom	x ($\sigma(x)$)	y ($\sigma(y)$)	z ($\sigma(z)$)
Fe1	0.1337 (2)	−0.2158	0.7302 (1)
Fe2	0.2341 (2)	−0.3141 (1)	0.8906 (1)
P1	0.2146 (3)	−0.1657 (2)	0.8803 (2)
P2	0.3321 (3)	−0.2784 (2)	0.7805 (2)
P3	0.4636 (3)	−0.4804 (2)	0.6069 (2)
O1	0.2416 (9)	−0.1465 (6)	0.6630 (6)
O11	−0.1372 (9)	−0.2294 (10)	0.7192 (8)
O12	0.1216 (15)	−0.0398 (9)	0.6438 (10)
O13	0.0498 (11)	−0.3043 (11)	0.5419 (7)
O21	0.0058 (11)	−0.3452 (8)	0.9487 (11)
O22	0.4320 (10)	−0.3271 (11)	1.0786 (8)
O23	0.2294 (15)	−0.5075 (7)	0.8460 (10)
N1	0.1445 (10)	−0.0969 (8)	0.9396 (8)
N2	0.4736 (9)	−0.2200 (7)	0.8152 (7)
C1	0.3470 (12)	−0.3790 (9)	0.7038 (8)
C2	0.4625 (12)	−0.4021 (8)	0.6943 (9)
C11	−0.0305 (12)	−0.2224 (10)	0.7264 (9)
C12	0.1325 (15)	−0.1112 (11)	0.6778 (11)
C13	0.0888 (12)	−0.2783 (11)	0.6171 (10)
C21	0.0947 (12)	−0.3315 (9)	0.9260 (11)
C22	0.3556 (13)	−0.3215 (11)	1.0042 (10)
C23	0.2288 (15)	−0.4325 (10)	0.8575 (11)
C111	0.2380 (22)	0.0536 (13)	0.9074 (16)
C112	0.2133 (15)	−0.0113 (10)	0.9841 (11)
C113	0.3330 (17)	−0.0333 (14)	1.0705 (13)
C121	−0.0826 (15)	−0.0363 (11)	0.8738 (13)
C122	0.0119 (13)	−0.1076 (10)	0.9375 (11)
C123	0.0029 (18)	−0.1157 (13)	1.0418 (13)
C211	0.7089 (13)	−0.2686 (12)	0.8831 (12)
C212	0.5799 (11)	−0.2489 (9)	0.9026 (10)
C213	0.6062 (14)	−0.1846 (12)	0.9890 (11)
C221	0.4927 (22)	−0.0529 (12)	0.7901 (17)
C222	0.4915 (18)	−0.1462 (12)	0.7516 (13)
C223	0.4891 (27)	−0.1664 (15)	0.6573 (15)
C311	0.3845 (11)	−0.5852 (8)	0.6186 (8)
C312	0.3908 (13)	−0.6145 (9)	0.7098 (9)
C313	0.3399 (14)	−0.6967 (10)	0.7213 (10)
C314	0.2835 (13)	−0.7537 (9)	0.6424 (11)
C315	0.2769 (13)	−0.7236 (10)	0.5521 (11)
C316	0.3250 (13)	−0.6382 (10)	0.5379 (9)
C317	0.2293 (18)	−0.8426 (12)	0.6587 (15)
C321	0.3852 (12)	−0.4363 (9)	0.4874 (9)
C322	0.4511 (14)	−0.3964 (11)	0.4322 (12)
C323	0.3909 (17)	−0.3518 (11)	0.3478 (12)
C324	0.2621 (16)	−0.3455 (10)	0.3110 (11)
C325	0.1909 (15)	−0.3868 (12)	0.3609 (12)
C326	0.2492 (13)	−0.4314 (11)	0.4489 (10)
C327	0.1912 (20)	−0.2949 (13)	0.2159 (12)
C331	0.6276 (11)	−0.5099 (9)	0.6161 (9)
C332	0.7272 (15)	−0.4484 (10)	0.6455 (13)
C333	0.8547 (13)	−0.4702 (11)	0.6467 (14)
C334	0.8798 (13)	−0.5522 (10)	0.6180 (11)
C335	0.7810 (13)	−0.6153 (10)	0.5919 (13)
C336	0.6579 (13)	−0.5950 (9)	0.5896 (10)
C337	1.0168 (14)	−0.5805 (14)	0.6213 (17)

Table VII. Selected Bond Distances (Å) and Angles (deg) for $[(i\text{-}Pr_2NP)_2HCOCHPpTo_3]Fe_2(CO)_6$

bond distances		bond angles	
Fe1–P1	2.277 (4)	P1–Fe1–P2	73.2 (1)
Fe1–P2	2.308 (4)	P1–Fe2–P2	76.6 (2)
Fe2–P1	2.212 (4)	P1–Fe1–Fe2	51.2 (1)
Fe2–P2	2.200 (4)	P2–Fe1–Fe2	50.7 (1)
Fe1–Fe2	2.747 (2)	P1–Fe2–Fe1	53.3 (1)
Fe1–C11	1.78 (1)	P2–Fe2–Fe1	54.2 (1)
Fe1–C12	1.73 (2)	Fe1–P1–N1	125.9 (4)
Fe1–C13	1.85 (1)	Fe2–P1–N1	129.2 (5)
Fe2–C21	1.74 (2)	Fe1–P2–Fe2	75.1 (1)
Fe2–C22	1.86 (1)	Fe1–P2–N2	126.4 (4)
Fe2–C23	1.82 (2)	Fe2–P2–N2	117.6 (4)
P1–N1	1.64 (1)	Fe1–P2–C1	109.8 (4)
P2–N2	1.74 (1)	Fe2–P2–C1	111.6 (4)
P2–C1	1.89 (1)	N2–P2–C1	111.4 (6)
C1–O1	1.29 (1)	P2–C1–C2	118.6 (9)
C1–C2	1.35 (2)	P2–C1–O1	114.6 (10)
C2–P3	1.73 (1)	C2–C1–O1	126.8 (12)
		C1–C2–P3	114.9 (9)
		C2–P3–C311	114.8 (6)
		C2–P3–C321	111.8 (6)
		C2–P3–C331	106.9 (6)

finement of the best angular positions for 15 independent reflections ($2\theta > 15°$) during normal alignment procedures using molybdenum radiation ($\lambda = 0.710\,69$ Å). Data (4102 independent points after removal of space group forbidden and redundant data) were collected at room temperature by using a variable scan rate, a θ–2θ scan mode, and a scan width of 1.2° below $K\alpha_1$ and 1.2° above $K\alpha_2$ to a maximum 2θ value of 50°. Backgrounds were measured at each side of the scan for a combined time equal to the total scan time. The intensities of three standard reflections were remeasured after every 97 reflections. As the intensities of these reflections showed less then 5% variation, corrections for decomposition were deemed unnecessary. Data were corrected for Lorentz, polarization, and background effects. Observed reflections [2648 with $I > 3.0\sigma(I)$] were used for solution of iron positions by direct methods using MULTAN 80.[8] P, C, N, and O positions were determined from a difference Fourier synthesis following refinement of the Fe positions. Refinement[9] of scale factor, positional, and isotropic thermal parameters for all atoms was carried out to convergence. Hydrogen positions for isopropyl, phenyl, and methylene hydrogen atoms were calculated by using idealized geometry. These were included but not refined in final cycles of refinement with fixed isotropic thermal parameters. Final cycles of least-squares refinement were completed with anisotropic thermal parameters [function minimized, $\sum(|F_o| - |F_c|)^2$] leading to a final agreement factor, $R = 5.8\%$ [$R = (\sum||F_o| - |F_c||/\sum|F_o|) \times 100$]. Scattering factors were taken from Cromer and Mann.[10] Anomalous dispersion corrections were made for Fe and P.[11] In the final stages of refinement a weight of $1/\sigma(F)^2$ was used. $R_w = 7.2\%$.

Results

The phosphonium methylides $R_3P{=}CH_2$ used in this work were generated by a standard method[6] involving deprotonation of the corresponding methylphosphonium salts with an alkyllithium in diethyl ether according to the following equation:

$$R_3PCH_3{}^+X^- + R'Li \rightarrow R_3P{=}CH_2 + R'H + LiX \qquad (2)$$

The reactions of $R_3P{=}CH_2$ (R = Me, Ph, pTo) with $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ (I) were performed in situ. The phosphorus-31 NMR spectra of the reaction mixtures indicated the formation of a new derivative exhibiting three widely spaced resonances. Elemental analysis of the air-stable yellow-orange solid products isolated from these reaction mixtures indicated the complexation of the lithium halide byproduct from eq 2. This complexed lithium halide was readily removed by passing a tetrahydrofuran solution through a silica gel column to give products of the stoichiometry $[(i\text{-}Pr_2NP)_2HCOCHPR_3]Fe_2(CO)_6$. Removal of the complexed lithium halide did not lead to significant changes in the NMR spectra. Pure $(Me_2N)_3P{=}CH_2$ isolated by vacuum distillation[7] was used for the reaction with $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ so that this system was free from lithium halide, thereby leading more readily to pure $[(i\text{-}Pr_2NP)_2HCOCHP(NMe_2)_3]Fe_2(CO)_6$.

The spectroscopic properties of the four derivatives $[(i\text{-}Pr_2NP)_2HCOCHPR_3]Fe_2(CO)_6$ (R = Me, Me_2N, Ph, pTo) listed in Tables I–IV suggest analogous structures for the four compounds but are inconsistent with formulation as the 1,2-oxaphosphetane intermediates (II in Figure 1) expected for a Wittig-type reaction. Therefore a structure determination by X-ray diffraction was undertaken by using the *p*-tolyl derivative $[(i\text{-}Pr_2NP)_2HCOCHPpTo_3]Fe_2(CO)_6$, since suitable single crystals of it could be more readily obtained than of the corresponding methyl or phenyl derivatives. The X-ray study indicated a phosphonium acylmethylide structure (IV in Figure 1 and Figures 2 and 3) similar to that found in the metal-free derivatives

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Table VIII. Bond Distances in (Acylmethylene)phosphoranes

compd	infrared ν(C=O),[a] cm^{-1}	distances[b] in RC(O)C(X)PR'$_3$ Unit, Å C—O	C—C	C—P	lit. refs
$[(i\text{-}Pr_2NP)_2HCOCHPpTo_3]Fe_2(CO)_6$	1422	1.29 (1)	1.35 (2)	1.73 (1)	this work
$PhC(O)C(Cl)PPh_3$	1470	1.301 (19)	1.361 (20)	1.736 (14)	12
$PhC(O)C(I)PPh_3$	1465	1.28 (6)	1.35 (7)	1.71 (5)	13
$MeOC(O)C(CH_2CO_2H)PPh_3$	1620	1.243 (6)	1.392 (6)	1.732 (4)	15
$MeOC(O)C(CH_2CO_2CMe_3)PPh_3$	1620	1.221 (6)	1.415 (7)	1.715 (2)	15
$MeOC(O)CHPPh_3$	1621	1.33 (2)	1.37 (3)	1.69 (3)	14

[a] See the cited references and also: Speziale, A. J.; Ratts, K. W. *J. Am. Chem. Soc.* **1963**, *85*, 2790. [b] Standard deviations are given in parentheses.

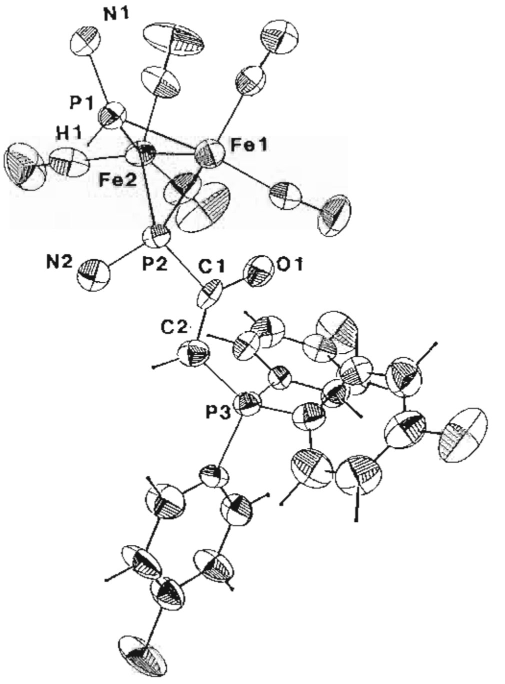

Figure 2. ORTEP diagram of $[(i\text{-}Pr_2NP)_2HCOCHPpTo_3]Fe_2(CO)_6$ with the isopropyl groups, one iron carbonyl group (C12–O12), and the labels on the phenyl groups omitted for clarity.

$PhC(O)C(X)PPh_3$ (X = Cl[12] and I[13]), $MeOC(O)CHPPh_3$,[14] and $MeOC(O)C(CH_2CO_2R)PPh_3$ (R = H[15] and Me_3C[15]). All of these structures contain a central RC(O)C(X)PR'$_3$ unit, which is the following resonance hybrid:

Va Vb

Table VIII compares the C—O, C—C, and C—P distances in the central RC(O)C(X)PR$_3$ units of all of these structures. Within experimental error these distances in $[(i\text{-}Pr_2NP)_2HCOCHPpTo_3]Fe_2(CO)_6$ (IV: R = pTo) including the $pTo_3P{=}C$ carbon–phosphorus multiple bond are seen to be the same as those in the other structures of this type. In addition note that the acyl C=O distances of 1.28 (6)–1.30 (2) Å in these structures where R = OCH_3 (Table VIII) are somewhat longer than the phosphorus-bridging carbonyl C=O distances of 1.185 (12), 1.23 (2), and 1.20 (1) Å in the derivatives $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ (I),[4] $(i\text{-}Pr_2NP)_3COFe_2(CO)_6$,[4] and $(i\text{-}Pr_2NP)(t\text{-}Bu_2P)COFe_2(CO)_6$,[1] respectively, in accord with the role of the Va ↔ Vb resonance in decreasing the C—O bond order.

The X-ray structure of $[(i\text{-}Pr_2NP)_2HCOCHpTo_3]Fe_2(CO)_6$ also indicates a typical Fe_2P_2 unit with one Fe–Fe bond (2.747 (2) Å) and four Fe–P bonds ranging from 2.200 (4) to 2.308 (4) Å but no P–P bond. One phosphorus–nitrogen bond (P1–N1) is seen to be equatorial and the other phosphorus–nitrogen bond (P2–N2) is seen to be axial relative to the bent Fe_2P_2 ring (Figures 2 and 3). The phosphorus–nitrogen bonds are anti to each other.

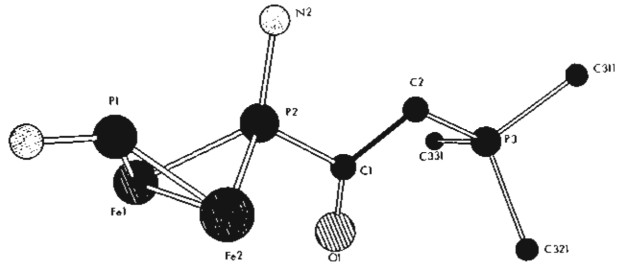

Figure 3. Drawing of the central portion of the $[(i\text{-}Pr_2NP)_2HCOCHPpTo_3]Fe_2(CO)_6$ molecule.

The spectroscopic properties of the $[(i\text{-}Pr_2NP)_2HCOCHPR_3]Fe_2(CO)_6$ derivatives are in accord with structure IV (Figure 1) found by X-ray diffraction. The infrared spectra in CH_2Cl_2 solution of all four derivatives exhibit four terminal ν(CO) frequencies in the range 2040–1940 cm^{-1} as well as a strong band at 1422 cm^{-1}, which can be assigned to the "acyl" carbonyl group in structure Va. The low value of this acyl carbonyl frequency is consistent with that found in other RC(O)C(X)PR'$_3$ derivatives where R $\neq$ OCH_3 (Table VIII) and again relates to the contribution of resonance structure Vb. The phosphorus-31 NMR spectra (Table II) exhibit the expected three resonances. The five-bond coupling constant between the R_3P phosphorus and the P–H phosphorus around δ 150 is seen to be negligible. The proton NMR spectra (Table III) exhibit a P–H resonance centered at δ ~5.9 with the expected large $|^1J(\text{P–H})|$ of 406 Hz as well as a readily observable $|^3J(\text{P–H})|$ of 22 Hz. The R_3PCH proton resonances appear in the range δ 3.8–4.4 depending upon the R group with a $|^2J(\text{P–H})|$ of 25 ± 3 Hz. The two carbon atoms of the RC(O)C(X)PR'$_3$ units in the $[(i\text{-}Pr_2NP)_2HCOCHPR_3]Fe_2(CO)_6$ derivatives are more difficult to observe in the carbon-13 NMR spectra than the resonances from the isopropyl, R group, and metal carbonyl carbons but have been observed in some cases (Table IV). Both the proton and carbon-13 NMR spectra of all four $[(i\text{-}Pr_2NP)_2HCOCHPR_3]Fe_2(CO)_6$ derivatives (Tables III and IV) indicate clearly the nonequivalent diisopropylamino groups required by the observed structure (IV in Figure 1).

There are four possible stereoisomers of the $[(i\text{-}Pr_2NP)_2HCOCHPR_3]Fe_2(CO)_6$ that can be classified by the locations of the two diisopropylamino substituents on the bent Fe_2P_2 ring as axial–axial, axial–equatorial, equatorial–axial, and equatorial–equatorial listing first the phosphorus atom bearing the carbonylmethylenephosphorane substituent. From this convention the structure of $[(i\text{-}Pr_2NP)_2HCOCHPpTo_3]Fe_2(CO)_6$ determined by X-ray diffraction corresponds to the axial–equatorial isomer (Figures 2 and 3). A question of interest is whether any of the other three stereoisomers of the $[(i\text{-}Pr_2NP)_2HCOCHPR_3]Fe_2(CO)_6$ derivatives can be detected in the reaction products. In this connection, the phosphorus-31 NMR spectrum of the crude reaction mixture from $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ and $pTo_3P{=}CH_2$ suggested the presence of a minor product from the observation of a second set of weaker $i\text{-}Pr_2NPHFe_2$ and R_3P phosphorus resonances (Table II); the

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$i\text{-Pr}_2\text{NPCFe}_2$ phosphorus resonance of the minor product was hidden under the corresponding resonance of the major product. This minor product could be one of the other three stereoisomers of $[(i\text{-Pr}_2\text{NP})_2\text{HCOCHPpTo}_3]\text{Fe}_2(\text{CO})_6$. The ratio of the minor to major product in the crude reaction mixture was 2:7. Furthermore, the $i\text{-Pr}_2\text{NPHFe}_2$ doublet splitting of 66 Hz in the minor product was very different from the corresponding 117-Hz doublet splitting of the major product. The phosphorus-31 resonances of the minor product disappeared during the subsequent purification and product isolation. The phosphorus-31 NMR spectrum of the crude reaction mixture from $(i\text{-Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ and $\text{Ph}_3\text{P}{=}\text{CH}_2$ in tetrahydrofuran but not in diethyl ether (Table II) also exhibited the resonances for a minor product with chemical shifts and coupling constants similar to those of the minor product from $(i\text{-Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ and $\text{pTo}_3\text{P}{=}\text{CH}_2$. No similar evidence was found for the formation of analogous minor products in the corresponding reactions of $(i\text{-Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ with the two other phosphonium methylides $\text{R}_3\text{P}{=}\text{CH}_2$ (R = Me and Me_2N). The similarity of the phosphorus–phosphorus coupling constants of the isolated stereoisomer of $[(i\text{-Pr}_2\text{NP})_2\text{HCOCHPpTo}_3]\text{Fe}_2(\text{CO})_6$ to those of the isolated stereoisomers of $[(i\text{-Pr}_2\text{NP})_2\text{HCOCHPR}_3]\text{Fe}_2(\text{CO})_6$ (R = Me, Me_2N, and Ph) suggests that the stereochemistries of the latter three products are the same as that of $[(i\text{-Pr}_2\text{NP})_2\text{HCOCHPpTo}_3]\text{Fe}_2(\text{CO})_6$ determined by X-ray diffraction.

Discussion

The phosphorus-bridging carbonyl group in $(i\text{-Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ (I) has been shown to be reactive toward phosphonium methylides of the type $\text{R}_3\text{P}{=}\text{CH}_2$ (R = Me, Me_2N, Ph, pTo). However, the ultimate result of this reaction is not the standard Wittig olefination product $[(i\text{-Pr}_2\text{NP})_2\text{C}{=}\text{CH}_2]\text{Fe}_2(\text{CO})_6$ (III in Figure 1). Instead, the observed product (IV in Figure 1) can be formed by hydrogen migration from carbon to phosphorus in an initially formed 1,2-oxaphosphetane (II in Figure 1) or the corresponding betaine analogous to intermediates in the standard Wittig olefination reaction.[2] In this way the observed formation of IV from $(i\text{-Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ (I) and $\text{R}_3\text{P}{=}\text{CH}_2$ can be related to the Wittig olefination reaction. The net result of this reaction sequence is the acylation of the ylide carbon of $\text{R}_3\text{P}{=}\text{CH}_2$ with the phosphorus-bridging carbonyl in $(i\text{-Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ (I). This reaction is significant in representing the first example of acylation by a phosphorus-bridging carbonyl group. However, the system studied in this paper has a number of special features including the ability of a phosphonium ylide to undergo 2 + 2 cycloaddition to a carbonyl group and the ability of the Fe_2P_2 structural unit in $(i\text{-Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ to pick up the hydrogen released in the acylation reaction. For these reasons a wide generality of acylation reactions of phosphorus-bridging carbonyl groups cannot be inferred from the results presented in this paper.

Note Added in Proof. Since this paper was accepted for publication a paper by Weber, Lücke, and Boese came to our attention: Weber, L.; Lücke, E.; Boese, R. *Chem. Ber.* **1989**, *122*, 809. Although the main emphasis of this paper is the reaction of $(i\text{-Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ with $\text{Me}_2\text{S(O)}{=}\text{CH}_2$ and the structure of the resulting methylene-insertion product $[(i\text{-Pr}_2\text{NPCH}_2)_2\text{CO}]\text{Fe}_2(\text{CO})_6$, this paper also describes the product $[(i\text{-Pr}_2\text{NP})_2\text{HCOCHPPh}_3]\text{Fe}_2(\text{CO})_6$ from the reaction of $\text{Ph}_3\text{P}{=}\text{CH}_2$ with $(i\text{-Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$. The spectroscopic properties reported by Weber, Lücke, and Boese for $[(i\text{-Pr}_2\text{NP})_2\text{HCOCHPPh}_3]\text{Fe}_2(\text{CO})_6$ are in essential agreement with those described in this paper. No X-ray crystallographic studies were reported by Weber, Lücke, and Boese on any $[(i\text{-Pr}_2\text{NP})_2\text{HCOCHPR}_3]\text{Fe}_2(\text{CO})_6$ derivatives.

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Supplementary Material Available: Listings of hydrogen positional parameters (Table I), anisotropic thermal parameters (Table 2), and bond angles (deg) and distances (Å) (Table 3) and a labeled ORTEP diagram for $[(i\text{-Pr}_2\text{NP})_2\text{HCOCHP}(\text{C}_6\text{H}_4\text{Me-}p)_3]\text{Fe}_2(\text{CO})_6$ (5 pages); a listing of F_o and F_c for $[(i\text{-Pr}_2\text{NP})_2\text{HCOCHP}(\text{C}_6\text{H}_4\text{Me-}p)_3]\text{Fe}_2(\text{CO})_6$ (32 pages). Ordering information is given on any current masthead page.