Transition-Metal-Substituted Acylphosphines and Phosphaalkenes. 7.[1] Phosphaalkenyl–Rhenium Complexes—A Novel Class of Compounds with P=C Bonding

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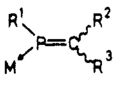
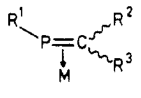
Treatment of $[(\eta^5\text{-}C_5Me_5)Re(CO)_2(NO)]BF_4$ with $LiPR(SiMe_3)$ in ether afforded the novel phosphaalkenyl complexes $(\eta^5\text{-}C_5Me_5)(CO)(NO)ReC(OSiMe_3){=}PR$ (R = $SiMe_3$, *t*-Bu, Ph). Analogously (*E*)-$(\eta^5\text{-}C_5H_5)$-$(CO)(NO)Re\text{-}C(OSiMe_3){=}P\text{-}t\text{-}Bu$ was obtained from $[(\eta^5\text{-}C_5H_5)Re(CO)_2(NO)]BF_4$ and $LiP(t\text{-}Bu)(SiMe_3)$. The course of the reaction was monitored by ^{31}P NMR spectroscopy and indicated formation of phosphinocarbonyl complexes $(\eta^5\text{-}C_5R'_5)(CO)(NO)ReC(O)P(R)SiMe_3$ via nucleophilic addition of phosphide to a CO ligand prior to the 1,3-silyl migration from phosphorus to oxygen. The molecular structures of $(\eta^5\text{-}C_5Me_5)(CO)(NO)ReC(OSiMe_3){=}P\text{-}t\text{-}Bu$ (**7b**) and $(\eta^5\text{-}C_5H_5)(CO)(NO)ReC(OSiMe_3){=}P\text{-}t\text{-}Bu$ (**8b**) were established by complete single-crystal diffraction studies. [**7b**: $P\bar{1}$ space group, $Z = 2$, $a = 7.629$ (2) Å, $b = 8.744$ (2) Å, $c = 18.798$ (9) Å, $\alpha = 79.29$ (3)°, $\beta = 78.85$ (3)°, $\gamma = 75.55$ (2)°. **8b**: $P\bar{1}$ space group, $Z = 2$, $a = 7.528$ (1) Å, $b = 9.847$ (2) Å, $c = 14.124$ (4) Å, $\alpha = 99.13$ (2)°, $\beta = 98.63$ (2)°, $\gamma = 107.82$ (1)°.]

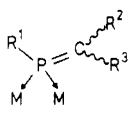
Compounds containing phosphorus–carbon multiple bonds are very interesting from both the theoretical as well as the preparative point of view.[2] The rapid development of the chemistry of such compounds also includes studies of their ligating properties. There are five possible coordination modes for a phosphaalkene (A–E), but the majority of complexes described so far in the literature belongs to type A, where the phosphaalkene acts as a terminal η^1-ligand via the phosphorus lone pair.[3]



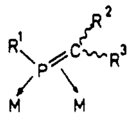
A η^1(P)



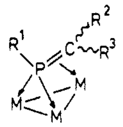
B η^2(P,C)



C $\eta^1(\mu_2\text{-P})$

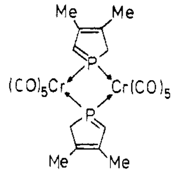


D $\eta^2(\mu_2\text{-P,C})$

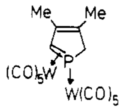


E $\eta^2(\mu_3)$

The η^2-complexation is known for several nickel, rhodium, and platinum compounds.[4] The compound $(Ph_3P)_2Pt[P(mesityl){=}CPh_2]$ is particularly interesting because of the subtle equilibrium between the η^1- and η^2-bonding modes.[5] Phosphaalkenes are also capable of acting as bridging two- or four-electron donors as shown in complexes 1 of type C and 2 of type D, respectively.[6] The coordination mode E is encountered in complex 3 where the phosphaalkene bonds to three metal atoms.[7] In complexes A–E the phosphaalkene $R^1P{=}CR^2R^3$ is incorporated as an intact building block.



1



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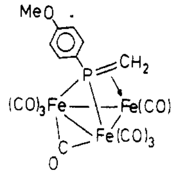
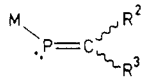
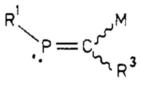


3

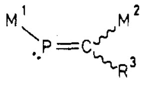
On the other hand, phosphaalkenes which are substituted by transition metals (as in I–V) instead of organic groups should be substantially different in character. In this paper we report full details on our synthetic approach to phosphaalkenyl complexes of the type II using transition-metal carbonyl cations and silylated lithium phosphides.[8,9] We also report the X-ray structure analyses of



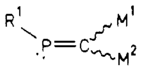
I



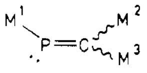
II



III



IV



V

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two phosphaalkenyl–rhenium complexes with different stereochemistry at the P=C double bond.

Experimental Section

General Information. Standard inert-atmosphere techniques were used for the manipulation of all reagents and reaction products. Infrared spectra were recorded on a Perkin-Elmer Model 597 spectrometer. The ^{1}H, ^{13}C, and ^{31}P NMR spectra were taken on a Varian XL 200 NMR spectrometer. Spectral standards were $\mathrm{SiMe_4}$ (^{1}H, ^{13}C) and 85% $\mathrm{H_3PO_4}$ (^{31}P). Chemical-ionization mass spectra were recorded on a Varian MAT 312 spectrometer. Osmometric molecular weight determinations were performed with a Knauer osmometer in $\mathrm{CH_2Cl_2}$. Elemental analyses were obtained from the Microanalytical Laboratory of the University Essen and from the Microanalytical Laboratory, Dornis and Kolbe, Mülheim, Germany.

Materials. The lithium phosphides $\mathrm{LiP(SiMe_3)_2 \cdot 2THF}$,[10] $\mathrm{LiP}(t\text{-Bu})(\mathrm{SiMe_3})$,[11] and $\mathrm{LiP(Ph)(SiMe_3)}$[11] as well as the complexes $[(\eta^5\text{-C}_5\mathrm{Me}_5)\mathrm{Re(CO)_2(NO)]BF_4}$[12] and $[(\eta^5\text{-C}_5\mathrm{H}_5)\mathrm{Re(CO)_2(NO)]BF_4}$[13] were prepared as described in the literature. All solvents were rigorously dried with an appropriate drying agent and distilled prior to use.

Preparation of Compounds. (*E*)-(η^5-C$_5$Me$_5$)(CO)(NO)ReC(OSiMe$_3$)=PSiMe$_3$ (7a). A solution of 1.650 g (5.04 mmol) of $\mathrm{LiP(SiMe_3)_2 \cdot 2THF}$ in 20 mL of ether was added dropwise and slowly to a stirred suspension of 2.490 g (5.04 mmol) of $[(\eta^5\text{-C}_5\mathrm{Me}_5)\mathrm{Re(CO)_2(NO)]BF_4}$ in 50 mL of ether at −78 °C. On warming to room temperature a dark red solution was obtained. This was stirred for 30 min and evaporated to dryness in vacuo, and the dark red solid residue was extracted with 40 mL of hexane. The filtered extract was concentrated to ca. 10 mL. While it stood for 12 h at −25 °C, dark red crystals were formed. After the mother liquor was pipetted off, the crystals were dried in vacuo. (*E*)-2-[carbonylnitrosyl(pentamethylcyclopentadienyl)rhenio]-2-(trimethylsiloxy)-1-(trimethylsilyl)-1-phosphaethene (**7a**): yield 0.75 g (25%); mp 88 °C; IR (hexane) 1980 s (ν(CO)), 1686 s (ν(NO)) cm^{-1}; IR (Nujol) 1980 s (ν(CO)), 1683 s (ν(NO)), 1265 m, 1258 s (δ(Si(CH$_3$)$_3$)), 1240 m, 1130 s (ν(SiOC)), 920 m, 860 s, 845 s (ρ-(Si(CH$_3$)$_3$)), 730 w, 688 w cm^{-1}; ^{1}H NMR (C$_6$D$_6$, 22 °C) δ 0.41 (d, ^3J(PH) = 3 Hz, 9 H, PSi(CH$_3$)$_3$), 0.42 (s, 9 H, OSi(CH$_3$)$_3$), 1.66 (s, 15 H, C$_5$(CH$_3$)$_5$); ^{13}C NMR (C$_6$D$_6$, 22 °C) δ 1.0 (s, PSi(CH$_3$)$_3$), 1.7 (s, OSi(CH$_3$)$_3$), 10.3 (s, C$_5$(*C*H$_3$)$_5$), 104.1 (s, *C*$_5$(CH$_3$)$_5$), 207.3 (d, ^3J(PC) = 19.7 Hz, ReCO), 252.5 (d, ^1J(PC) = 113.5 Hz, C=P); ^{31}P NMR (C$_6$D$_6$, 22 °C) δ 212.4 (s). Anal. Calcd for $\mathrm{C_{18}H_{33}NO_3PReSi_2}$ (584.8): C, 36.97; H, 5.67; N, 2.40; Re, 31.81. Found: C, 36.41; H, 6.02; N, 2.41; Re, 31.72. Molecular weight: found 585 (MS/CI); 539 (osmometrically in $\mathrm{CH_2Cl_2}$).

(*Z*)-(η^5-C$_5$Me$_5$)(CO)(NO)ReC(OSiMe$_3$)=P-*t*-Bu (7b). Analogously a 0.48 M ethereal solution of LiP(*t*-Bu)(SiMe$_3$) (9.1 mL, 4.37 mmol) was allowed to react with 2.160 g (4.37 mmol) of $[(\eta^5\text{-C}_5\mathrm{Me}_5)\mathrm{Re(CO)_2(NO)]BF_4}$ suspended in 50 mL of ether to yield 0.750 g (30%) of red crystalline (*Z*)-1-*tert*-butyl-2-[carbonylnitrosyl(pentamethylcyclopentadienyl)rhenio]-2-(trimethylsiloxy)-1-phosphaethene (**7b**): mp 64 °C; IR (hexane) 1971 s (ν(CO)), 1688 s (ν(NO)) cm^{-1}; IR (Nujol) 1968 s (ν(CO)), 1675 s (ν(NO)), 1358 m, 1260 m, 1250 m (δ(Si(CH$_3$)$_3$)), 1050 s (ν(SiOC)), 980 m, 860 s, 850 s (ρ(Si(CH$_3$)$_3$)), 818 w, 760 w, 755 w, 720 w, 690 w cm^{-1}; ^{1}H NMR (C$_6$D$_6$, 22 °C) δ 0.52 (d, ^5J(PH) = 1.7 Hz, 9 H, OSi(CH$_3$)$_3$), 1.51 (d, ^3J(PH) = 10.7 Hz, 9 H, PC(CH$_3$)$_3$), 1.63 (s, 15 H, C$_5$(CH$_3$)$_5$); ^{13}C NMR (C$_6$D$_6$, 22 °C) δ 1.9 (d, ^4J(PC) = 8.4 Hz, OSi(CH$_3$)$_3$), 10.0 (s, C$_5$(*C*H$_3$)$_5$), 31.7 (d, ^2J(PC) = 12.8 Hz, C(*C*H$_3$)$_3$), 33.8 (d, ^1J(PC) = 39.0 Hz, *C*(CH$_3$)$_3$), 104.2 (s, *C*$_5$(CH$_3$)$_5$), 211.0 (s, ReCO), 241.9 (d, ^1J(PC) = 80.7 Hz, P=C); ^{31}P NMR (C$_6$D$_6$, 22 °C) δ 271.5 (s). Anal. Calcd for $\mathrm{C_{19}H_{33}NO_3PReSi}$ (568.7): C, 40.13; H, 5.85; N, 2.46; Re, 32.74. Found: C, 40.27; H, 5.56; N, 2.46; Re, 32.64. Molecular weight: found 570 (MS/CI); 525 (osmometrically in $\mathrm{CH_2Cl_2}$).

(*E*)-(η^5-C$_5$Me$_5$)(CO)(NO)ReC(OSiMe$_3$)=PPh (7c). Analogously, a 0.23 M ethereal solution of LiP(Ph)(SiMe$_3$) (20.2 mL, 4.65 mmol) reacted with a suspension of 2.300 g (4.65 mmol) of $[(\eta^5\text{-C}_5\mathrm{Me}_5)\mathrm{Re(CO)_2(NO)]BF_4}$ in 50 mL of ether to afford 1.020 g (37%) of dark red crystalline (*E*)-2-[carbonylnitrosyl(pentamethylcyclopentadienyl)rhenio]-1-phenyl-2-(trimethylsiloxy)-1-phosphaethene (**7c**): mp 99 °C; IR (hexane) 1973 s (ν(CO)), 1692 s (ν(NO)) cm^{-1}; IR (Nujol) 3070 w, 3060 w, 1970 s (ν(CO)), 1680 s (ν(NO)), 1430 w, 1262 m, 1252 s (δ(Si(CH$_3$)$_3$)), 1168 s (ν(SiOC)), 1160 sh, 1030 m, 935 m, 855 s (ρ(Si(CH$_3$)$_3$)), 765 w, 755 w, 732 m, 699 m cm^{-1}; ^{1}H NMR (C$_6$D$_6$, 22 °C) δ 0.12 (s, 9 H, OSi(CH$_3$)$_3$)), 1.71 (s, 15 H, C$_5$(CH$_3$)$_5$), 7.10–7.24 (m, 3 H, *m*- + *p*-H(phenyl)), 7.63–7.69 (m, 2 H, *o*-H(phenyl)); ^{13}C NMR (C$_6$D$_6$, 22 °C) δ 0.4 (s, OSi(CH$_3$)$_3$), 9.9 (s, C$_5$(*C*H$_3$)$_5$), 94.2 (s, *C*$_5$(CH$_3$)$_5$), 132.8 (d, ^2J(PC) = 11.0 Hz, *o*-C(phenyl)), 148.6 (d, ^1J(PC) = 60.2 Hz, i-C(phenyl)), 210.5 (d, ^3J(PC) = 21.7 Hz, ReCO), 230.7 (d, ^1J(PC) = 106.1 Hz, C=P); ^{31}P NMR (C$_6$D$_6$, 22 °C) δ 194.4 (s). Anal. Calcd for $\mathrm{C_{21}H_{29}NO_3PReSi}$ (588.7): C, 42.84; H, 4.97; N, 2.38. Found: C, 42.47; H, 5.02; N, 2.14. Molecular weight: found 589 (MS/CI).

(*E*)-(η^5-C$_5$H$_5$)(CO)(NO)ReC(OSiMe$_3$)=P-*t*-Bu (8b). Analogously, a 0.25 M ethereal solution of LiP(*t*-Bu)(SiMe$_3$) (10.1 mL, 2.52 mmol) reacted with a suspension of 1.17 g (2.52 mmol) of $[(\eta^5\text{-C}_5\mathrm{H}_5)\mathrm{Re(CO)_2NO]BF_4}$ in 25 mL of ether to give 0.640 g (54%) of dark red crystalline (*E*)-1-*tert*-butyl-2-[carbonyl(cyclopentadienyl)nitrosylrhenio]-2-(trimethylsiloxy)-1-phosphaethene (**8b**): IR (hexane) 1991 s (ν(CO)), 1706 s (ν(NO)) cm^{-1}; IR (Nujol) 3356 w, 3115 w, 3092 w, 1990 s, 1967 s, 1949 sh, 1926 sh (ν(CO)), 1702 s (ν(NO)), 1419 w, 1355 m, 1264 m, 1253 s (δ-(Si(CH$_3$)$_3$)), 1202 m, 1165 s (ν(SiOC)), 1064 w, 1018 w, 1003 w, 924 m, 840 s (ρ(Si(CH$_3$)$_3$) and π(CH)$_{\mathrm{ring}}$), 756 m, 691 w, 612 w, 592 w, 571 m, 520 w, 510 m, 495 m, 461 m cm^{-1}; ^{1}H NMR (C$_6$D$_6$, 22 °C) δ 0.38 (s, 9 H, OSi(CH$_3$)$_3$), 1.45 (d, ^3J(PH) = 9.0 Hz, 9 H, PC(CH$_3$)$_3$, 4.88 (s, 5 H, C$_5$H$_5$); ^{13}C NMR (C$_6$D$_6$, 22 °C) δ 1.1 (s, OSi(CH$_3$)$_3$), 29.6 (d, ^2J(PC) = 11.0 Hz, C(*C*H$_3$)$_3$), 40.4 (d, ^1J(PC) = 47.4 Hz, *C*(CH$_3$)$_3$), 93.3 (s, C$_5$H$_5$), 203.9 (d, ^3J(PC) = 22.8 Hz, ReCO), 210.0 (d, ^1J(PC) = 104.9 Hz, P=C); ^{31}P NMR (C$_6$D$_6$, 22 °C) δ 250.1 (s). Anal. Calcd for $\mathrm{C_{14}H_{23}NO_3PReSi}$ (498.6): C, 33.73; H, 4.65; N, 2.81. Found: C, 33.66; H, 4.41; N, 2.91. Molecular weight: found 500 (MS/CI).

X-ray Structure Determination of [(*Z*)-(η^5-C$_5$Me$_5$)(CO)(NO)ReC(OSiMe$_3$)=P-*t*-Bu (7b) and (*E*)-(η^5-C$_5$H$_5$)(CO)(NO)ReC(OSiMe$_3$)=P-*t*-Bu (8b). The crystals of **7b** and **8b** were sealed under nitrogen in capillaries and mounted on a Syntex R3 four-circle diffractometer, using graphite-monochromated Mo Kα radiation, 2θ–ω data collections with 96 step scans, and subsequent profile fitting with a learnt profile:[14a,b] structure solutions with Patterson and Fourier methods, using Shelxtl[14c] on a Nova 3/12 computer (Data General); structure refinements with block-cascade methods and idealized rigid groups for the Cp ring of **8b** and for the hydrogen atoms, using the 1.2-fold of the orthogonalized U_{ij} tensor of the corresponding C atom as the isotropic temperature factor. Further data are listed in Table I.

Results and Discussion

Becker found in the reaction between pivaloyl chloride and disilylated phosphines (or phosphides) a general synthesis for the novel class of phosphaalkenes (eq 1).[2b,15]

$$t\text{-BuC(O)Cl} + \mathrm{M'P(R)(SiMe_3)} \xrightarrow[-\mathrm{M'Cl}]{} [t\text{-BuC(O)P(R)(SiMe_3)}] \rightarrow (\mathrm{Me_3SiO})(t\text{-Bu})\mathrm{C{=}PR} \quad (1)$$

$$\mathrm{M'} = \mathrm{Li, Me_3Si};\ \mathrm{R} = \mathrm{H, Me_3Si}, \text{alkyl, aryl}$$

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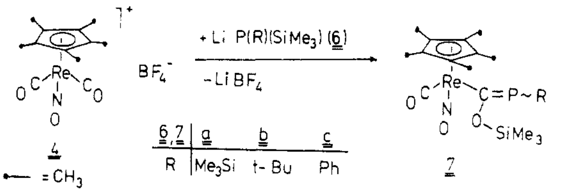
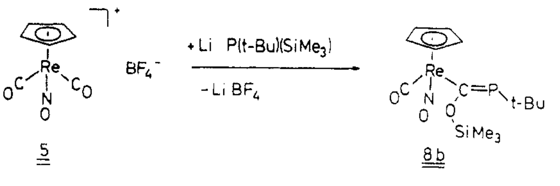
Table I. Crystallographic Data for the X-ray Diffraction Study of 7b and 8b

	7b	8b
cryst dimens	0.31 × 0.19 × 0.08 mm	0.20 × 0.18 × 0.15 mm
temp, °C	−155	23
cell dimens		
a, Å	7.629 (2)	7.528 (1)
b, Å	8.744 (2)	9.847 (2)
c, Å	18.798 (9)	14.124 (4)
α, deg	79.29 (3)	99.13 (2)
β, deg	78.85 (3)	98.63 (2)
γ, deg	75.55 (2)	107.82 (1)
V, Å^3	1178.9 (7)	962.0 (4)
space group	$P\bar{1}$	$P\bar{1}$
Z	2	2
D_{calcd}, g/cm^3	1.60	1.72
μ, cm^{-1}	55.8	68.3
2θ range	3–55	3–65
no. of independent intensities	5155	6969
no. of obsvn ($F_o \geq 3.5\sigma(F)$)	4991	5945
emp absorp corr		
merging *R* before/after corr, %	17.28/3.01	9.8/1.8
min/max transmission	0.379/0.943	0.015/0.050
R value	0.033	0.030
R_w value ($w^{-1} = \sigma^2(F) + GF^2$)	0.034	0.032
G	0.00025	0.00029
max residual electron density, e/Å^3	0.58	0.82

We intended to transfer a reaction sequence of this kind from organic carbonyl compounds to transition-metal carbonyls. Instead of pivaloyl chloride we employed the electrophilic organometallic carbonyls [(η^5-C_5Me_5)$(CO)_2$(NO)Re]BF_4 (**4**) and [(η^5-C_5H_5)$(CO)_2$(NO)Re]BF_4 (**5**). The silylated lithium phosphides LiP$(SiMe_3)_2$·2THF (**6a**), LiP(*t*-Bu)($SiMe_3$) (**6b**), and LiP(Ph)($SiMe_3$) (**6c**) react with an ethereal suspension of **4** at −78 °C to give an orange-yellow solution which turns reddish brown on warming to room temperature. The novel phosphaalkenyl–rhenium complexes **7a–c** are isolated as dark red, air-sensitive, and diamagnetic crystals. Analogously the extremely air-sensitive complex **8b** is obtained from treatment of **5** with LiP(*t*-Bu)($SiMe_3$).

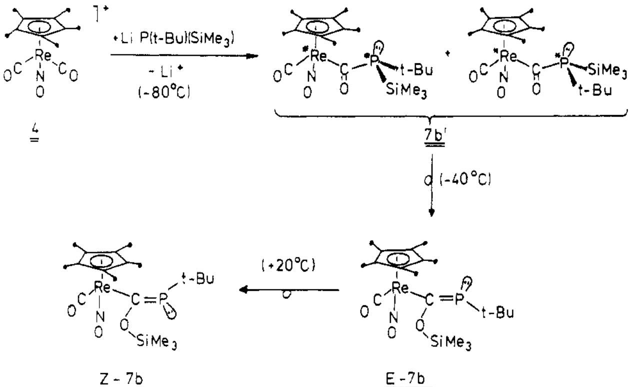


(2)



The products **7a–c** and **8b** were initially characterized by elemental analyses and spectroscopic methods (IR, ^{1}H, ^{13}C, and ^{31}P NMR, MS). Osmometrical molecular weight determinations in CH_2Cl_2 as well as chemical ionization mass spectra revealed the monomeric character of the compounds. The ^{31}P NMR spectra displayed singlets (δ_P 194.4–271.7) in the expected low-field region.

Scheme I



Doublets in the ^{13}C NMR spectra at δ_C 210–252.5 (^1J(PC) = 80.7–113 Hz) are due to the resonances of the ^{13}C nuclei of the C═P unit. The stereochemistry at the P═C double bond of **7a–c** and **8b** can be deduced from the ^{13}C NMR spectra. It is known that nuclei of substituents at the carbon atom of the P═C bond are more strongly coupled to phosphorus when they are arranged in a cis fashion to the phosphorus lone pair.[16] Singlets for the $(^{13}CH_3)_3SiO$ groups and doublets for the CO ligands (δ_C 203.9–210.5 (^3J(PC) = 19.7–22.8 Hz)) of **7a**, **7c**, and **8b** are consistent with the presence of *E* isomers, whereas a singlet for the ReCO group (δ_C 211.0) and doublet for the $(^{13}CH_3)_3SiO$ group (δ_C 1.9 (^4J(PC) = 8.4 Hz)) reveal **7b** to be the *Z* isomer. These results are confirmed by the X-ray analyses of **7b** and **8b** (vide infra).

It is interesting that only in the ^{1}H NMR spectra of *Z* configurated **7b** are the protons of the $(CH_3)_3SiO$ function (δ_H 0.52) split into a doublet (^5J(PH) = 1.7 Hz). Singlets are registered for the corresponding protons in the compounds **7a**, **7c**, and **8b** (δ_H 0.12–0.42). The Re(CO)(NO) group is recognizable by strong bands at 1971–1991 cm^{-1} (ν(CO)) and 1686–1706 cm^{-1} (ν(NO)) in the IR spectra (hexane) of **7a–c** and **8b**. A medium-strong band at 1050 cm^{-1} in **7b** (Nujol) is readily assigned to the ν(SiOC) mode. In **7a**, **7c**, and **8c** this vibration appears at significantly higher energy (1130–1168 cm^{-1}) which indicates some delocalization of an oxygen lone pair into the P═C bond (see also the corresponding C1–O1 distances in **7b** and **8b**).

The reaction of **4** with **6a,b** can be monitored by ^{31}P NMR spectroscopy. Thus a mixture of **4** and **6a** at −80 °C in ether gives rise to a singlet at δ_P −15.07 which is due to the phosphinocarbonyl complex (η^5-C_5Me_5)(CO)(NO)ReC(O)P$(SiMe_3)_2$ (**7a′**). The previously synthesized (η^5-C_5Me_5)$(CO)_2$FeC(O)P$(SiMe_3)_2$ exhibits a singlet at δ_P 6.2 (C_6D_6).[17] At −40 °C a small singlet appears at δ_P 212.0, indicating the beginning rearrangement to the final product **7a**. A broad singlet is registered at δ_P 39.3 when **4** and **6b** are reacted in ether solution. At −60 °C this resonance, slightly shifted to δ_P 43.2, is accompanied by a sharp singlet at δ_P 236.3. At −30 °C the spectrum is characterized by three sharp singlets at δ_P 47.35, 236.3, and 269.8. Above −20 °C the high-field signal diminishes in intensity, and at −10 °C it can no longer be detected. In its place the singlet at δ_P 240.1 increases in intensity, but at room temperature it diminishes in favor of the signal at δ_P 272.8. After 5 h, only this resonance, due to the final product (*Z*)-**7b**, is recorded.

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Table II. Atomic Coordinates (×10^4) and Isotropic Temperature Parameters (pm^2 × 10^{-1}) for 7b and 8b

atom	x	y	z	U,[a] Å^2
		7b		
Re1	3543 (1)	144 (1)	2095 (1)	19 (1)
P1	1620 (2)	4262 (1)	2361 (1)	29 (1)
Si1	1467 (2)	2597 (1)	4080 (1)	32 (1)
O1	2633 (4)	1838 (3)	3332 (2)	33 (1)
O2	1817 (4)	486 (4)	774 (2)	31 (1)
O3	676 (5)	−1340 (4)	3199 (2)	46 (1)
N1	2359 (4)	463 (4)	1342 (2)	26 (1)
C1	2491 (5)	2273 (4)	2587 (2)	25 (1)
C2	1487 (5)	4836 (4)	1357 (2)	25 (1)
C3	−106 (6)	4291 (5)	1163 (3)	31 (1)
C4	3255 (6)	4250 (5)	853 (3)	32 (1)
C5	1066 (6)	6681 (5)	1251 (3)	35 (1)
C6	2087 (7)	944 (7)	4823 (3)	43 (2)
C7	−1056 (7)	3054 (7)	4066 (3)	44 (2)
C8	2253 (9)	4356 (7)	4214 (3)	56 (2)
C9	5815 (5)	−2095 (4)	2267 (2)	25 (1)
C10	6146 (5)	−1374 (4)	1522 (2)	22 (1)
C11	6551 (5)	160 (4)	1510 (2)	22 (1)
C12	6457 (5)	371 (4)	2258 (2)	24 (1)
C13	5974 (5)	−992 (5)	2727 (2)	27 (1)
C14	5561 (6)	−3757 (5)	2539 (3)	35 (1)
C15	6188 (6)	−2083 (5)	850 (2)	29 (1)
C16	7204 (5)	1204 (5)	834 (2)	30 (1)
C17	6891 (6)	1767 (5)	2495 (3)	33 (1)
C18	5918 (7)	−1347 (6)	3539 (2)	38 (2)
C19	1710 (5)	−746 (5)	2792 (2)	28 (1)
		8b		
Re1	−69 (1)	642 (1)	3269 (1)	54 (1)
P1	−2857 (2)	1791 (1)	1849 (1)	64 (1)
Si1	2663 (2)	4602 (1)	3044 (1)	61 (1)
C1	−583 (5)	2165 (4)	2442 (3)	55 (1)
C2	−2871 (7)	2931 (5)	901 (3)	76 (2)
C3	−2165 (8)	4565 (5)	1353 (4)	85 (2)
C4	−1691 (11)	2599 (8)	164 (4)	111 (3)
C5	−4975 (9)	2483 (7)	385 (5)	112 (3)
C6	1630 (8)	5383 (6)	4014 (4)	85 (2)
C7	4679 (6)	4046 (5)	3543 (4)	75 (2)
C8	3518 (8)	5931 (6)	2273 (5)	88 (2)
C9	471 (6)	−383 (4)	1783 (2)	91 (2)
C10	−1116	−1401	2009	86 (2)
C11	−464	−1795	2887	82 (2)
C12	1526	−1022	3203	84 (2)
C13	2104	−149	2521	88 (2)
N1	1212 (6)	1841 (4)	4386 (3)	72 (1)
C14	−2414 (7)	374 (6)	3699 (4)	80 (2)
O1	938 (4)	3200 (3)	2267 (2)	63 (1)
O2	−3773 (6)	173 (6)	4004 (4)	122 (2)
O3	2140 (7)	2558 (4)	5179 (3)	114 (2)

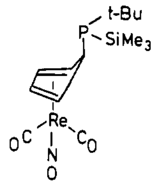
[a] Equivalent isotropic U, calculated as one-third of the trace of the orthogonalized U_{ij} tensor.

An interpretation of these data is depicted in Scheme I. Again the first step of the reaction must involve the generation of phosphinocarbonyl complexes **7b′** via the nucleophilic addition of the phosphide to a carbonyl ligand. The broad signal at δ_P 39.3 (−80 °C) may reflect an equilibrium between the two diastereomers of **7b′**. At −40 °C 1,3-SiMe$_3$ migration from phosphorus to oxygen yields the E isomer, which rearranges to the final product (Z)-**7b** during the course of several hours at room temperature. When the reaction mixture is freed from solvent at −40 °C, the IR spectrum of the residue features a low-energy C–O stretch (1580 cm^{-1}) which is consistent with the presence of **7b′**.

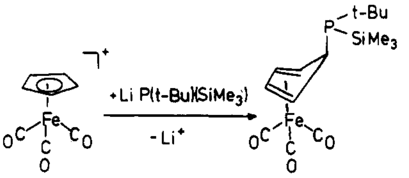
Table III. Bond Lengths (Å) and Selected Bond and Torsions Angles (deg) of 7b

	Bond Lengths		
Re1–N1	1.766 (4)	Re1–C1	2.138 (4)
Re1–C9	2.287 (3)	Re1–C10	2.292 (3)
Re1–C11	2.347 (4)	Re1–C12	2.362 (4)
Re1–C13	2.310 (4)	Re1–C19	1.932 (4)
P1–C1	1.704 (4)	P1–C2	1.877 (4)
Si1–O1	1.667 (3)	Si1–C6	1.852 (5)
Si1–C7	1.870 (5)	Si1–C8	1.858 (7)
O1–C1	1.399 (5)	O2–N1	1.211 (5)
O3–C19	1.140 (5)	C2–C3	1.536 (7)
C2–C4	1.523 (5)	C2–C5	1.547 (5)
C9–C10	1.426 (5)	C9–C13	1.451 (7)
C9–C14	1.495 (6)	C10–C11	1.445 (6)
C10–C15	1.499 (6)	C11–C12	1.436 (6)
C11–C16	1.500 (5)	C12–C13	1.428 (5)
C12–C17	1.503 (7)	C13–C18	1.494 (6)
	Bond Angles		
N1–Re1–C1	104.2 (1)	Re1–N1–O2	168.2 (3)
N1–Re1–C19	95.2 (2)	Re1–C1–P1	140.7 (2)
C1–Re1–C19	86.4 (2)	Re1–C1–O1	106.4 (2)
C1–P1–C2	112.3 (2)	P1–C1–O1	112.8 (3)
Si1–O1–C1	132.8 (2)		
	Torsions Angles		
Cp–Re1–C1–O1	−67.5	Cp–Re1–C1–P1	110.4

The reaction of **5** and **6b** seems to be more complicated. At −60 °C a singlet at δ_P 23.9 is recorded which is shifted to δ_P 24.8 upon warming up to −20 °C. At this temperature a new signal at δ_P 52.8 appears which increases in favor of that at δ_P 24.8, and at 0 °C this high-field signal is no longer observable. In the low-field region, characteristic for phosphaalkenes, a signal is recorded at δ_P 284.7. Warming to 20 °C leads to the complete disappearance of the high-field singlet, and the spectrum is now dominated by two intense singlets at δ_P 249.8 and 285.7. After five more hours only the resonance at δ_P 249.8, due to the final product (E)-**8b**, remains. It is therefore invoked that the other low-field resonance is caused by the Z isomer (Z)-**8b** and that the signal at ca. 50 ppm correponds to a phosphinocarbonyl complex. The nature of the first intermediate with the ^{31}P resonance at ca. 24 ppm is not fully understood at the moment. It is possible that the phosphide primarily adds to the cyclopentadienyl ring of the cation to afford the η^4-cyclopentadienyl phosphine complex **10**. Precedent for this addition can be found in the very recently reported synthesis of the closely related complex **11**.[18] Attempts to isolate the intermediates of all of these reactions failed.



10



11

(3)

The X-ray structure analysis of **7b** and **8b** fully confirm the conclusions derived from the spectroscopic data. The results of the structural determinations are shown in Figure 1. Positional parameters for the complexes are given in Table II, and derived distances and angles are presented

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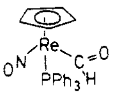
Table IV. Bond Lengths (Å) and Selected Bond and Torsions Angles (deg) of 8b

	Bond Lengths		
Re1-C1	2.130 (5)	Re1-C9	2.329 (5)
Re1-C10	2.303 (4)	Re1-C11	2.290 (5)
Re1-C12	2.307 (6)	Re1-C13	2.331 (6)
Re1-N1	1.752 (4)	Re1-C14	1.909 (6)
P1-C1	1.689 (4)	P1-C2	1.880 (6)
Si1-C6	1.850 (7)	Si1-C7	1.846 (6)
Si1-C8	1.860 (7)	Si1-O1	1.670 (3)
C1-O1	1.365 (5)	C2-C3	1.526 (7)
C2-C4	1.525 (10)	C2-C5	1.536 (8)
N1-O3	1.205 (5)	C14-O2	1.143 (8)
	Bond Angles		
C1-Re1-N1	99.9 (2)	P1-C1-Re1	116.6 (2)
C1-Re1-C14	91.5 (2)	O1-C1-Re1	118.9 (3)
N1-Re1-C14	91.0 (2)	O3-N1-Re1	173.9 (4)
C1-P1C2	109.1 (2)	O2-C14-Re1	175.4 (6)
P1-C1-O1	123.3 (3)	Si1-O1-C1	130.2 (3)
	Torsions Angles		
Cp-Re1-C1-O1	-79.1	Cp-Re1-C1-P1	88.5

in Tables III and IV. Both complexes are phosphaalkenes with comparable C=P double bond lengths (**7b**, 1.704 (4) Å; **8b**, 1.689 (4) Å). The C=P distances in localized phosphaalkenes range from 1.67 to 1.72 Å.[19] There are no significant differences in the ReC1 distances in both species (**7b**, 2.128 (4) Å; **8b**, 2.130 (5) Å), which are longer than the rhenium–formyl carbon distance in **12** (2.055 (10) Å).[20] The rhenium–acyl bond length in [(CO)$_5$Re(p-COC$_6$H$_4$Cl)][21] is 2.22 Å, and the average rhenium–(acyl/carbene) bond length in Lukehart's cyclic [(CO)$_4$Re[C(Me)OHOCMe] is 2.16 Å.[22]



12

The C1–O1 distance in **7b** (1.399 (5) Å) resembles that of a C(sp^2)O single bond (1.41 Å)[23] whereas the corresponding bond is **8b** is considerably shorter (1.365 (5) Å). This is rationalized by the resonance of an oxygen lone pair with the C=P double bond. However, the observed C=P distances do not reflect this,[24] but IR evidence for a strengthened C1–O1 bond in **8b** is given by the ν(SiOC) stretch (ν = 1165 cm^{-1}) at markedly higher energy than in **7b** (ν = 1050 cm^{-1}) (vide supra).

Clearly both complexes differ in the configuration at the C=P double bond. We assume that the steric bulk of the C$_5$Me$_5$ ring ligand accounts for the Z geometry in **7b**. The ring forces the Me$_3$Si group toward the phosphorus atom. Severe steric congestion between the cis-oriented Me$_3$Si and the *tert*-butyl groups causes the latter to shift to the other side of the double bond into the neighborhood of the rhenium. Evidently the less bulky substituents SiMe$_3$ (in **7a**) and Ph (in **7c**) are tolerated in the cis position to the Me$_3$SiO group.

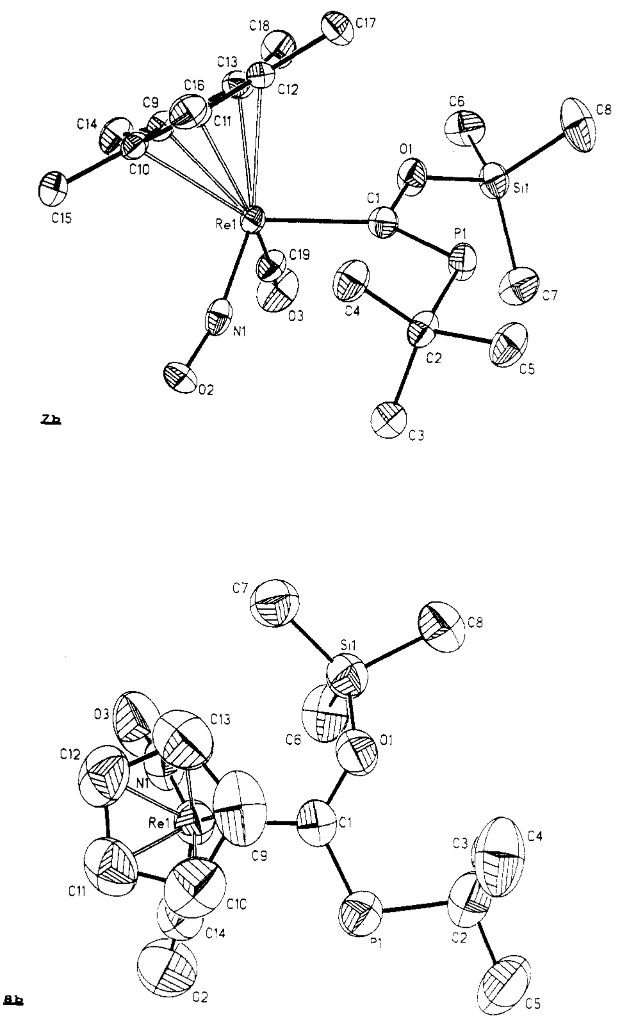


Figure 1. The molecular structures of (η^5-C$_5$Me$_5$)(CO)(NO)-ReC(OSiMe$_3$)=P-t-Bu (**7b**) and (η^5-C$_5$H$_5$)(CO)(NO)ReC-(OSiMe$_3$)=P-t-Bu (**8b**).

The proximity of the bulky (η^5-C$_5$Me$_5$)(CO)(NO)Re and *tert*-butyl groups in **7b** has the following consequences. (i) Rotation of the C$_5$Me$_5$Re fragment around the Re–C1 bond and away from the *tert*-butyl group provided some release of the steric crowding. (ii) In **7b** the angles C1P1C2 (112.3 (2)°) and ReC1P1 (140.7 (2)°) are widened significantly as compared to those in **8b** (109.1 (2)° and 116.2 (2)°, respectively). In **7b** the angles ReC1O1 (106.4 (2)°) and O1C1P1 (112.8 (3)°) are compressed in comparison to those in **8b** (118.9 (3)° and 123.3 (9)°, respectively). (iii) The angle C1ReN1 in **7b** (104.2 (1)°) is also significantly larger than the one in **8b** (99.9 (2)°). Also, the deviation from linearity of the ReNO fragment in **7b** (168.2 (3)°) is more pronounced than in **8b** (173.9 (4)°).

On the other hand, the angles SiO1C1 in both compounds are comparable (**7b**, 132.8 (2)°; **8b**, 130.2 (3)°). The ReC(CO) distances (**7b**, 1.932 (4) Å; **8b**, 1.909 (6) Å) are, within experimental error, comparable with those in Herrmann's Re$_2$(η^5-C$_5$Me$_5$)$_2$(CO)$_4$(μ-O) (1.860 (12)–1.895 (12) Å).[25] The ReN(NO) bond lengths (**7b**, 1.766 (4) Å; **8b**, 1.752 (4) Å) correspond well with those in **12** (1.777 (8)

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Å)[20] and (η^5-C_5H_5)(PPh_3)(NO)$ReCH_2Ph$ (1.749 (7) Å)[26] and deserve no comment.

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Registry No. 4, 86497-29-2; 5, 31960-40-4; 6 (R = $SiMe_3$), 59624-91-8; 6 (R = *t*-Bu), 89982-51-4; 6 (R = Ph), 79908-20-6; **7a**, 93984-99-7; **7b**, 93984-98-6; **7c**, 93985-00-3; **8b**, 101011-66-9.

Supplementary Material Available: Listings of structure factor amplitudes for **7b** and **8b** (72 pages). Ordering information is given on any current masthead page.

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Semibridging Interactions and Conformational Equilibria in Methoxymethylidyne Cluster Complexes. Syntheses, Spectroscopic, and X-ray Crystallographic Studies on $CoFe_2(\mu\text{-}H)(\mu_3\text{-}COCH_3)(CO)_7(\eta\text{-}C_5H_5)$, $Fe_2Ni(\mu_3\text{-}COCH_3)(\mu_3\text{-}CO)(CO)_6(\eta\text{-}C_5H_5)$, and $AuCoFe_2(\mu_3\text{-}COCH_3)(\mu_3\text{-}CO)(CO)_6(PPh_3)(\eta\text{-}C_5H_5)$

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Treatment of $Fe_3(\mu\text{-}H)(\mu\text{-}COCH_3)(CO)_{10}$ (1) in toluene at 363 K with either $Co(CO)_2(\eta\text{-}C_5H_5)$ or $[Ni(CO)(\eta\text{-}C_5H_5)]_2$ affords $CoFe_2(\mu\text{-}H)(\mu_3\text{-}COCH_3)(CO)_7(\eta\text{-}C_5H_5)$ (2) or $Fe_2Ni(\mu_3\text{-}COCH_3)(\mu_3\text{-}CO)(CO)_6(\eta\text{-}C_5H_5)$ (3), respectively. Formation of 3 was accompanied by minor quantities of $FeNi(\mu\text{-}CO)_2(CO)(\eta\text{-}C_5H_5)_2$ (4) and $Fe_3(\mu_3\text{-}COCH_3)(\mu\text{-}CO)_2(CO)_6(\eta\text{-}C_5H_5)$ (5). Complexes 2–5 were characterized by IR, NMR, and mass spectroscopies, with single-crystal X-ray diffraction studies on 2 and 3. Crystal data for 2: $P2_1/a$, a = 13.901 (1) Å, b = 8.207 (1) Å, c = 14.725 (2) Å, β = 85.973 (8)°, Z = 4, final R (R_w) values 0.028 (0.036) for 1990 independent observed data. The $CoFe_2$ triangle is asymmetrically capped by a μ_3-$COCH_3$ group (Fe(1)–C(8) = 1.871 (4) Å; Fe(2)–C(8) = 1.877 (4) Å; Co(1)–C(8) = 2.001 (4) Å), the carbonyl group on Co(1) showing slight semibridging interactions with the two iron atoms (Fe(1)···C(7) = 2.559 (4) Å; Fe(2)···C(7) = 2.629 (5) Å). Crystal data for 3: $P\bar{1}$, a = 7.930 (3) Å, b = 8.338 (1) Å, c = 13.474 (2) Å, α = 96.97 (1)°, β = 98.97 (2)°, γ = 107.12 (2)°, Z = 2, final R (R_w) values 0.030 (0.040) for 3482 independent observed data. The $NiFe_2$ triangle is nearly symmetrically capped by a μ_3-carbonyl ligand (Ni(1)–C(7) = 1.944 (3) Å; Fe(1)–C(7) = 2.056 (3) Å; Fe(2)–C(7) = 2.065 (3) Å), the μ_3-$COCH_3$ group being approximately equidistant from the three metal atoms (Ni(1)–C(8) = 1.959 (3) Å; Fe(1)–C(8) = 1.902 (3) Å; Fe(2)–C(8) = 1.888 (3) Å). Treatment of 2 with $AuCH_3(PPh_3)$ in toluene at 363 K afforded $AuCoFe_2(\mu_3\text{-}COCH_3)(\mu_3\text{-}CO)(CO)_6(PPh_3)(\eta\text{-}C_5H_5)$ (6), thereby replacing μ-H by μ-$AuPPh_3$. Crystal data for 6: $P2_1/n$, a = 13.669 (3) Å, b = 14.313 (5) Å, c = 16.665 (4) Å, β = 103.12 (2)°, Z = 4, final R (R_w) values 0.024 (0.031) for 4257 independent observed data. The C(7)–Fe(1) and C(7)–Fe(2) interactions (2.322 (6) and 2.362 (6) Å, respectively) are noticeably greater than in 2. Variable-temperature ^{13}C NMR spectra on 2, 3, and 6 indicate conformational equilibria in solution, with two distinct species observable in IR studies on 3. These data indicate there to be a soft potential energy surface relating the μ_3 and semi μ_3 bonding configurations of the methoxymethylidyne group about the trimetallic cluster.

Introduction

There is currently great interest in the chemistry of cluster complexes containing alkylidyne ligands, due partly to the putative involvement of such intermediates in the catalytic reduction of CO by H_2,[1] with strong evidence also existing for similar species in the chemisorption of hydrocarbons at metal surfaces.[2] In contrast to the rapidly developing chemistry of cluster species containing the μ-CR (R = aryl, alkyl) ligand,[3] relatively little work has been reported on corresponding alkoxy-substituted derivatives. This is in spite of the availability of facile, high yield synthetic routes to such complexes via O-alkylation of bridging carbonyl ligands in anionic clusters, e.g., reaction of $[M_3(\mu\text{-}H)(\mu\text{-}CO)(CO)_{10}^-]$ with CH_3SO_3F to give $M_3(\mu\text{-}H)(\mu\text{-}COCH_3)(CO)_{10}$ (**1a**, M = Fe;[4] **1b**, M = Ru;[5] **1c**, M = Os[6]). Reports in the literature on the reactivity of cluster-bound μ-COR groups are sparse however. Shapley et al. have achieved alkylidyne carbon functionalization by

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