Synthesis, Structure, and Coordination Chemistry of P-Acyl-, P-Thiocarbamoyl-, and P-Dithiocarboxyl-Substituted Phosphaalkenes $R(X)C{-}P{=}C(NMe_2)_2$ (R = Ph, *t*Bu, $SSiMe_3$, $N(Ph)SiMe_3$; X = O, S)†

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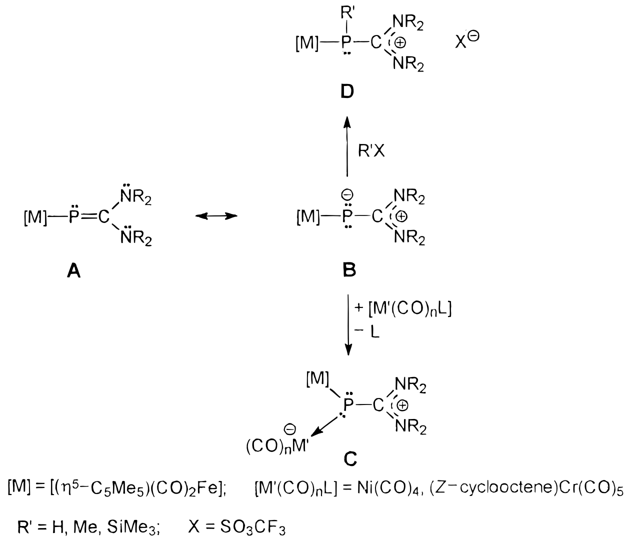
Reaction of $Me_3SiP{=}C(NMe_2)_2$ (**1**) with pivaloyl chloride and benzoyl chloride afforded the acylated phosphaalkenes $RC(O)P{=}C(NMe_2)_2$ **2a** (R = *t*Bu) and **2b** (R = Ph). Carbon disulfide and phenyl isothiocyanate were inserted into the P−Si bond of **1** to give the functionalized phosphaalkenes $R(X)C{-}P{=}C(NMe_2)_2$ **2c** [$R(X)C = Me_3Si{-}S(S)C$] and **2d** [$R(X)C = Ph(Me_3Si)N(S)C$]. Heating **2c** and **2d** with $(CO)_5MBr$ (M = Mn, Re) in toluene at 50−80 °C led to complexes $[X = \overline{CSM(CO)_3\text{-}\mu\text{-}P}C(NMe_2)_2]_2$ **3c** (M = Mn, X = S), **3d** (M = Mn, X = NPh), **4c** (M = Re, X = S), and **4d** (M = Re, X = NPh). The X-ray structure analysis of **2c** showed extensive π-delocalization of electron density from phosphorus into the C=S group. The structure determination of **4d** revealed the molecule as a tricyclic system with an anti orientation of the peripheric four-membered rings. The organophosphorus fragment serves as η^2(P,S)-μ(P) bridging ligand, a coordination mode without precedence in phosphaalkene chemistry.

Introduction

The vast majority of phosphaalkenes show a polarity $P^{\delta+}\ C^{\delta-}$ of the PC double bond as anticipated by the different electronegativities of carbon and phosphorus.[2,3] There are, however, a number of phosphaalkenes comprising $RP{=}C(NMe_2)_2$ [R = H,[4] $SiMe_3$,[5,6] $(\eta^5\text{-}C_5Me_5)(CO)_2Fe$[7]], $CF_3P{=}C(NR_2)F$ (R = Me, Et),[8] and the phosphatriafulvenes $RP{=}\overline{C{-}C(tBu){=}C}(tBu)$ (R = $SiMe_3$, 2,4,6-$Me_3C_6H_2$)[9] where an inverse polarity $P^{\delta-}\ C^{\delta+}$ of the multiple bond is encountered.

During the course of our continuing studies on P-metallophosphaalkenes of the type $(\eta^5\text{-}C_5Me_5)(CO)_2M{-}P{=}C(NR_2)_2$ (M = Fe, Ru; R = Me, Et), we observed a marked elongation of the PC bond upon η^1-coordination to 16 VE complex fragments such as $[Ni(CO)_3]$ or $[Cr(CO)_5]$.[10] This finding suggests a description of the bonding situation in metallophosphaalkenes by two canonical formulas **A** and **B**, the zwitterion of which is stabilized by η^1-ligation of the molecule to a metal center (**C**) (Scheme 1).

Scheme 1



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† Dedicated to Professor Peter Jutzi on the occasion of his 60th birthday.

(1) Part 36: Weber, L.; Dembeck, G.; Stammler, H.-G.; Neumann, B. *Eur. J. Inorg. Chem.* **1998**, 579.

(2) Review: Schoeller, W. W. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Thieme: Stuttgart 1990; pp 5−31.

(3) Reviews: (a) Appel, R. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Thieme: Stuttgart 1990; pp 157−219. (b) Appel, R.; Knoll, F. *Adv. Inorg. Chem.* **1989**, *33*, 259−361. (c) Markovskii, L. N.; Romanenko, V. D. *Tetrahedron* **1989**, *45*, 6019−6090. (d) Dillon, K. B.; Mathey, F.; Nixon, J. F. *Phosphorus: The Carbon Copy*; Wiley: Chichester, 1998; pp 88−127.

(4) Chernega, A. N.; Ruban, A. V.; Romanenko, V. D.; Markovskii, L. N.; Korkin, A. A.; Antipin, M. Y.; Struchkov, Y. T. *Heteroat. Chem.* **1991**, *2*, 229.

(5) Markovskii, L. N.; Romanenko, V. D.; Pidvarko, T. I. *Zh. Obshch. Khim.* **1982**, *52*, 1925; *Chem. Abstr.* **1982**, *97*, 216330h.

(6) Weber, L.; Kaminski, O. *Synthesis* **1995**, 158.

(7) Weber, L.; Kaminski, O.; Stammler, H.-G.; Neumann, B.; Romanenko, V. D. *Z. Naturforsch.* **1993**, *48B*, 1784.

(8) Grobe, J.; Le Van, D.; Nienstedt, J.; Krebs, B.; Dartmann, M. *Chem. Ber.* **1988**, *121*, 655.

(9) Fuchs, E. P. O.; Heydt, H.; Regitz, M.; Schoeller, W. W.; Busch, T. *Tetrahedron Lett.* **1989**, *30*, 5111.

(10) (a) Weber, L.; Quasdorff, B.; Stammler, H.-G.; Neumann, B. *Chem. Eur. J.* **1998**, *4*, 465. (b) Quasdorff, B. Ph.D. Thesis, Universität Bielefeld, 1997.

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Moreover protonation, alkylation, and silylation occur at the phosphorus atom to give α-phosphanyl carbenium ions (**D**).[11]

We are interested in the polarity and chemical behavior of nonmetalated phosphaalkenes of the type RC(O)−P=C(NMe$_2$)$_2$. If in these molecules a significant accumulation of electron density at phosphorus occurs, delocalization of negative charge into the organic carbonyl substituents should be possible.

This paper focuses on the synthesis, structure, bonding, and coordination chemistry of P-acyl-, P-dithiocarboxyl-, and P-thiocarbamoyl derivatives of inversely polarized phosphaalkenes.

Experimental Section

All operations were performed with standard Schlenk techniques in an oxygen-free Ar atmosphere. Solvents were dried by standard methods and freshly distilled under argon. Infrared spectra were recorded on a Bruker FT-IR IFS66 spectrometer, and the ^{1}H, ^{13}C, and ^{31}P NMR spectra were taken on Bruker AM Avance DRX 500, Bruker AC 250P, and Bruker AC 100 instruments; standards: SiMe$_4$ (^{1}H, ^{13}C) and external 85% H$_3$PO$_4$ (^{31}P). Elemental analyses were performed in the microanalytical laboratory of the University of Bielefeld. Mass spectra were obtained with a VG Autospec sector-field mass spectrometer (micromass).

Phosphaalkene Me$_3$SiP=C(NMe$_2$)$_2$ [6] and the complexes Mn(CO)$_5$Br,[12] Re(CO)$_5$Br,[13] and Re$_2$(CO)$_6$Br$_2$thf$_2$ [13] were synthesized according to the literature. Carbon disulfide, phenyl isothiocyanate, pivaloyl chloride, and benzoyl chloride were purchased commercially.

Preparation of Compounds. *t*BuC(O)P=C(NMe$_2$)$_2$ (2a). A solution of pivaloyl chloride (0.14 g, 1,13 mmol) in 10 mL of *n*-pentane was added dropwise to a chilled solution (−30 °C)-of Me$_3$SiP=C(NMe$_2$)$_2$ (0.23 g, 1.13 mmol) in 40 mL of *n*-pentane, whereupon a light yellow precipitate separated. The chilled slurry was filtered, and the filter cake was washed with 50 mL of cold *n*-pentane (−30 °C). After drying in vacuo, **2a** was obtained as a light yellow analytically pure powder (0.17 g, 70%). ^{1}H NMR (C$_6$D$_6$, 22 °C) δ: 1.43 (s, 9H, *t*Bu), 2.60 (s, 12H, NMe$_2$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 22 °C) δ: 28.4 [s, C(*C*H$_3$)$_3$], 42.7 [s, N(CH$_3$)$_2$], 47.6 [d, $^2J_{PC}$ = 41.0 Hz, *C*(CH$_3$)$_3$], 201.4 [d, $^1J_{PC}$ = 80.5 Hz, P=*C*(NMe$_2$)$_2$], 231.4 [d, $^1J_{PC}$ = 90.8 Hz, *t*Bu*C*(O)]. ^{31}P{^{1}H} NMR (C$_6$D$_6$, 22 °C) δ: 26.4 s. IR (KBr, cm^{-1}) ν: 2946 m, 2927 sh, 2857 w, 1563 vs [ν(CO)], 1527 s, 1467 m, 1443 m, 1414 w, 1380 sh, 1367 s, 1351 m, 1267 m, 1209 w, 1148 m, 1135 w, 1111 w, 1092 m, 1057 w, 1026 m, 941 s, 921 s, 876 w, 804 w, 679 w, 646 w, 614 w, 516 w, 449 w. MS/EI *m/z*: 216 (M$^+$), 131 [P=C(NMe$_2$)$_2{}^+$], 100 [C(NMe$_2$)$_2{}^+$], 85 (*t*BuCO$^+$), 57 (*t*Bu$^+$), 44 (NMe$_2{}^+$). Anal. Calcd for C$_{10}$H$_{21}$N$_2$OP (216.26): C, 55.54; H, 9.79; N, 12.95. Found: C, 53.74; H, 9.76; N, 12.62.

PhC(O)P=C(NMe$_2$)$_2$ (2b). Analogously, 0.24 g (77%) of pure yellow powderous **2b** was synthesized by combination of 0.19 g (1.32 mmol) of benzoyl chloride and 0.27 g (1.32 mmol) of Me$_3$SiP=C(NMe$_2$)$_2$ in 40 mL of *n*-pentane. ^{1}H NMR (C$_6$D$_6$, 22 °C) δ: 2.68 (s, 12H, NMe$_2$), 7.18 (m, 3H, *m*- and *p*-phenyl-H), 8.35 (m, 2H, *o*-phenyl-H). ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ: 42.9 [s, N(CH$_3$)$_2$], 126.4 (s, phenyl-C), 126.5 (s, phenyl-C), 130.7 (s, *o*-phenyl-C), 145.0 (d, $^2J_{PC}$ = 49.3 Hz, *i*-phenyl-C), 199.3 [d, $^1J_{PC}$ = 78.5 Hz, P=*C*(NMe$_2$)$_2$], 215.6 [d, $^1J_{PC}$ = 78.7 Hz, Ph*C*(=O)]. ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ: 31.3 s. IR (film, CsI, cm^{-1}) ν: 2926 m, 1583 w, 1546 s [ν(CO)], 1492 m, 1464 m, 1441 m, 1404 w, 1369 s, 1268 m, 1193 m, 1166 m, 1147 m, 1108 m, 1088 s, 1058 sh, 925 m, 899 s, 876 m, 771 m, 733 w, 696 m, 653 w, 632 m, 544 w. MS/EI *m/z*: 236 (M$^+$), 131 [PC(NMe$_2$)$_2{}^+$], 44 (NMe$_2{}^+$). Anal. Calcd for C$_{12}$H$_{17}$N$_2$OP (236.25): C, 61.01; H, 7.25; N, 11.86. Found: C, 60.46; H, 7.83; N, 11.76.

Me$_3$SiSC(S)P=C(NMe$_2$)$_2$ (2c). A solution of carbon disulfide (0.07 mL, 82.3 mg, 1.08 mmol) in 10 mL of *n*-pentane was added dropwise to a cold solution (−50 °C) of Me$_3$Si-P=C(NMe$_2$)$_2$ (0.22 g, 1.08 mmol) in 30 mL of *n*-pentane. A yellow precipitate occurred immediately, which was filtered and washed with 50 mL of cold *n*-pentane (−30 °C). Yield: 0.26 g (86.1%) of pure yellow powderous **2c**. ^{1}H NMR (C$_6$D$_6$, 22 °C) δ: 0.59 (s, 9H, SiMe$_3$), 2.65 (s, 12H, NMe$_2$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 22 °C) δ: 2.2 [s, Si(CH$_3$)$_3$], 43.3 [s, N(CH$_3$)$_2$], 193.7 [d, $^1J_{PC}$ = 87.2 Hz, P=*C*(NMe$_2$)$_2$], 234.5 (br, PCS$_2$). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 22 °C) δ = 145 br. IR (Nujol, cm^{-1}) ν: 1624 m, 1589 m, 1553 s, 1510 sh, 1488 s, 1402 w, 1366 s, 1300 m, 1265 s, 1258 s, 1249 s [δ(SiMe$_3$)], 1183 s, 1162 w, 1140 w, 1106 m, 1085 s [ν(C=S)], 1072 sh, 957 w, 906 w, 879 w, 845 s [ρ(SiMe$_3$)], 755 m, 696 m, 621 w, 566 w, 508 w. MS/EI *m/z*: 280 (M$^+$), 149 (Me$_3$SiSCS$^+$). Anal. Calcd for C$_9$H$_{21}$N$_2$P$_2$S$_2$Si (280.46): C, 38.54; H, 7.55; N, 9.99. Found: C, 38.21; H, 7.35; N, 10.46.

Ph(Me$_3$Si)N−C(S)P=C(NMe$_2$)$_2$ (2d). A solution of phenyl isothiocyanate (0.17 g, 1.26 mmol) in 10 mL of *n*-pentane was dropped into a cold solution (−30 °C) of Me$_3$SiP=C(NMe$_2$)$_2$ (0.26 g, 1.26 mmol) in 30 mL of *n*-pentane to afford pure **2d** as an orange powder (0.31 g, 72%). ^{1}H NMR (C$_6$D$_6$, 22 °C) δ: 0.57 (s, 9H, SiMe$_3$), 2.61 (s, 12H, NMe$_2$), 6.9−7.2 (m, 5H, phenyl-H). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 22 °C) δ: 3.5 [s, Si(CH$_3$)$_3$], 43.2 [s, N(CH$_3$)$_2$], 127.0 s, 128.0 s, 129.3 s, 148.2 (s, phenyl-C), 198.1 (d, $^1J_{PC}$ = 72.1 Hz, P=*C*(NMe$_2$)$_2$], 231.5 [d, $^1J_{PC}$ = 72.3 Hz, N(C=S)P]. ^{31}P{^{1}H} NMR (C$_6$D$_6$, 22 °C) δ: 82.8 s. IR (KBr, cm^{-1}) ν: 2946 w, 2930 w, 2893 w, 1589 w, 1519 m, 1482 m, 1462 w, 1448 w, 1404 w, 1265 vs, 1250 sh [δ(SiMe$_3$)], 1193 s, 1139 w, 1114 m, 1094 w, 1037 vs [ν(C=S)], 999 w, 940 w, 912 w, 873 w, 847 s [ρ(SiMe$_3$)], 712 w, 698 w, 622 m, 567 w, 520 w. MS/EI *m/z*: 339 (M$^+$), 131 [P=C(NMe$_2$)$_2{}^+$]. 44 (NMe$_2{}^+$). Anal. Calcd for C$_{15}$H$_{26}$N$_3$PSSi (339.52): C, 53.06; H, 7.72; N, 12.38. Found: C, 53.06; H, 7.60; N, 12.41.

[S=C−S−Mn(CO)$_3$-*μ*-PC(NMe$_2$)$_2$]$_2$ (3c). A solution of 1.23 mmol of **2c** in 40 mL of toluene was prepared from 0.25 g of Me$_3$SiP=C(NMe$_2$)$_2$ and 0.09 g of carbon disulfide at −50 °C. After warmup to 20 °C, solid (CO)$_5$MnBr (0.34 g, 1.23 mmol) was added and the suspension was heated to 50 °C, whereupon a color change from light red to dark red and the separation of a deep-red precipitate occurred. After 1 h of stirring it was cooled to 20 °C, and the slurry was filtered. The filter cake was washed with cold CH$_2$Cl$_2$ (5 × 10 mL, 0 °C) to afford pure **3c** as a red-violet powder (0.32 g, 73.4%). ^{1}H NMR (CD$_2$Cl$_2$, 22 °C) δ: 3.23 (s, NMe$_2$). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 22 °C) δ: 121 s. IR (KBr, cm^{-1}) ν: 1994 [s, ν(CO)], 1908 [s, ν(CO)], 1700 w, 1653 w, 1550 m, 1507 w, 1496 w, 1458 w, 1387 m, 1262 w, 1090 w, 941 m, 668 m, 630 m, 517 w. Anal. Calcd for C$_{18}$H$_{24}$Mn$_2$N$_4$O$_6$P$_2$S$_4$ (692.50): C, 31.22; H, 3.49; N, 8.09. Found: C, 31.56; H, 3.54; N, 7.50.

[PhN=C−S−Mn(CO)$_3$-*μ*-PC(NMe$_2$)$_2$]$_2$ (3d). A sample of solid (CO)$_5$MnBr (0.34 g, 1.23 mmol) was added at 20 °C to the solution of 1.23 mmol of **2d** (prepared from 0.25 g of Me$_3$SiP=C(NMe$_2$)$_2$ and 0.17 g of phenyl isothiocyanate) in 40 mL of toluene. The slurry was stirred at 70 °C until all (CO)$_5$MnBr went into solution. Stirring was continued for 2 h, whereupon an orange precipitate separated. After being cooled to 20 °C, it was filtered and the filter cake was washed with cold CH$_2$Cl$_2$ (3 × 10 mL, 0 °C). The orange powder was crystallized from hot CH$_2$Cl$_2$ to give 0.28 g (56.2%) of **3d**. The product is insoluble in arenes, ethers, and saturated hydrocarbons and only slightly soluble in CH$_2$Cl$_2$. ^{1}H NMR (CD$_2$Cl$_2$, 22 °C) δ: 3.38 (s, 12H, NMe$_2$), 7.07 (m, 3H, *m*- and *p*-phenyl-H), 7.37 (m, 2H, *o*-phenyl-H). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 22 °C) δ: −17 (s, br). IR (KBr, cm^{-1}) ν: 2000 [w, ν(CO)], 1982 [s, ν(CO)], 1903 [s, ν(CO)], 1894 [s, ν(CO)], 1889 sh, 1559 [s, ν(C=N)],

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[11] Weber, L.; Scheffer, M.; Stammler, H.-G.; Neumann, B., manuscript in preparation.

[12] Abel, E. W.; Wilkinson, G. *J. Chem. Soc. (London)* **1959**, 1501.

[13] Vitali, D.; Calderazzo, F. *Gazz. Chim. Ital.* **1972**, *102*, 586.

1499 w, 1484 w, 1464 w, 1446 w, 1387 m, 1260 w, 1113 w, 913 w, 868 w, 763 w, 696 w, 663 m, 633 m, 516 w. MS/LSIMS, nitrobenzyl alcohol matrix *m*/*z*: 810 (M$^+$). Anal. Calcd for $C_{30}H_{34}Mn_2N_6O_6P_2S_2{\cdot}CH_2Cl_2$ (895.47): C, 41.58; H, 4.05; N, 9.39. Found: C, 41.83; H, 4.14; N, 9.57.

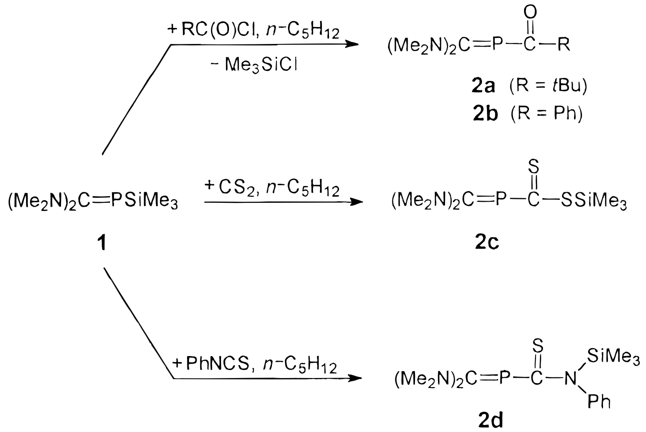
$[S{=}\overline{C{-}S{-}Re(CO)_3\text{-}\mu\text{-}P}C(NMe_2)_2]_2$ (4c). Path 1. A sample of solid $(CO)_5ReBr$ (0.54 g, 1.32 mmol) was added to a solution of 1.32 mmol of **2c** (prepared from 0.27 g of $Me_3SiP{=}C(NMe_2)_2$ and 0.10 g of CS_2 in 40 mL of toluene. The slurry was stirred at 70 °C until all $(CO)_5ReBr$ went into solution. After 30 min, a red precipitate occurred, and the slurry was stirred for another 60 min. Cooling the deep-red slurry to 20 °C and filtration afforded dark red **4c**, which was washed with cold CH_2Cl_2 (5 × 10 mL, 0 °C). Yield: 0.52 g (82.5%).

Path 2. A yellow slurry of 0.98 mmol of **2c** in 40 mL of *n*-pentane was produced by combination of 0.20 g of Me_3Si-$P{=}C(NMe_2)_2$ and 0.075 g of carbon disulfide. At −20 °C, a solution of $Re_2(CO)_6Br_2(thf)_2$ (0.41 g, 0.49 mmol) in 10 mL of THF was added dropwise. Warming to room temperature led to the formation of a red precipitate. After 60 min of stirring it was filtered, and the filter cake was washed with cold CH_2Cl_2 (4 × 20 mL, 0 °C) to give 0.32 g (68%) of **4c** as a red powder. The product is insoluble in common organic solvents and only slightly soluble in CH_2Cl_2. ^1H NMR (CD_2Cl_2, 22 °C) δ: 3.29 (s, br, NMe_2). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 22 °C) δ: 60 (s, br). IR (KBr, cm^{-1}) ν: 1998 [s, ν(CO)], 1889 [s, ν(CO)], 1696 w, 1653 w, 1550 m, 1495 w, 1458 w, 1384 m, 1261 w, 1154 w, 1107 m, 945 m, 923 m, 865 w, 637 w, 621 w, 517 w. Anal. Calcd for $C_{18}H_{24}N_4O_6P_2Re_2S_4$ (955.04): C, 22.64; H, 2.53; N, 5.87. Found: C, 22.13; H, 2.77; N, 5.66.

$[PhN{=}\overline{C{-}S{-}Re(CO)_3\text{-}\mu\text{-}P}C(NMe_2)_2]_2$ (4d). A sample of solid $(CO)_5ReBr$ (0.40 g, 0.98 mmol) was added to a solution of 0.98 mmol of **2d** (prepared in situ from 0.20 g of $Me_3SiP{=}C(NMe_2)_2$ and 0.13 g of phenyl isothiocyanate) in 40 mL of toluene. The slurry was stirred at 80 °C, whereupon the color changed to deep-red and an orange precipitate separated. After 2 h, the slurry was cooled to 20 °C and filtered. The filter cake was washed with cold CH_2Cl_2 (3 × 10 mL, 0 °C) to afford 0.25 g (47.5%) of pure orange **4d**. Single crystals were grown from hot CH_2Cl_2 upon slow cooling to ambient temperature. ^1H NMR (CD_2Cl_2, 22 °C) δ: 3.42 (s, 12H, NMe_2), 7.03 (m, 2H, phenyl-H), 7.06 (m, 1H, phenyl-H), 7.35 (m, 2H, phenyl-H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 22 °C) δ: −116 s. IR (KBr, cm^{-1}) ν: 1995 [s, ν(CO)], 1909 [s, ν(CO)], 1890 [s, ν(CO)], 1564 [m, ν(N=C)], 1550 [m, ν(N=C)], 1484 w, 1463 w, 1446 w, 1388 w, 1260 w, 1158 w, 1114 w, 915 w, 868 w, 767 w, 694 w, 663 w, 517 w. MS/LSIMS, nitrobenzyl alcohol matrix *m*/*z*: 1073 (M$^+$). Anal. Calcd for $C_{30}H_{34}N_6O_6P_2Re_2S_2$ (1073.10): C, 33.58; H, 3.19; N, 7.83. Found: C, 33.41; H, 2.92; N, 7.43.

X-ray Crystal Structure Determination of 2c. Single crystals of **2c** were grown from toluene at −30 °C. A red needlelike crystal with the approximate dimensions of 0.2 × 0.2 × 0.45 mm^3 was measured on a Siemens SMART CCD area detector system with three-axis geometry with Mo *K*α radiation at 173 K. Crystal data and refinement details: Crystal system monoclinic, cell dimensions a = 9.4986(6) Å, b = 11.8038(7) Å, c = 13.4494(8) Å, β = 98.3100(10)°, V = 1492.11(16) Å^3 (refined from 5356 reflections) Z = 4, d_{calcd} = 1.248 g cm^{-3}, μ = 0.520 mm^{-1}, space group $P2_{1/n}$, hemisphere data collection in ω at 0.3° scan width in three runs with 606, 435 and 230 frames (ϕ = 0, 88, and 180°) at a detector distance of 5 cm (2 θ_{max} = 54°), data reduction with the SAINT program (V4.028 Siemens)by which more than 93.5% of the data are covered, empirical absorption correction with redundant data (SADABS program, Siemens) max/min transmission 1.000/0.770; 8294 intensities collected, 3194 unique (R_{int} = 0.0218); structure solution and refinement on F^2 with SHELX97, 143 parameters, hydrogen atoms treated as riding groups with a 1.5-fold isotropic U value of the equivalent U value of the corresponding C atom. R1 = 0.0397; wR2 = 0.0724 for all data, $w^{-1} = \sigma^2(F_o^{\,2}) + (0.0357P)^2 + 0.35P$, where $P = [\max(F_o^{\,2}, 0) + 2F_c^{\,2}]/3$, maximum/minimum residual electron densities 0.293 and −0.240 eÅ^{-3}.

Scheme 2



X-ray Crystal Structure Determination of 4d. Single crystals of **4d** were grown by slow cooling a saturated boiling CH_2Cl_2 solution to ambient temperature. A yellow crystal with the approximate dimensions of 0.22 × 0.22 × 0.16 mm^3 was measured on a Bruker AXS SMART CCD area detector system with a three-axis goniometer and with Mo *K*α radiation at 183 K. Crystal data and refinement details: cell dimensions a = 9.3004(4) Å, b = 10.0027(4) Å, c = 12.8497(5) Å, α = 106.112(1)°, β = 104.544(1)°, γ = 98.936(1)°, V = 1078.6(1) Å^3 (refined from all reflections $>20\sigma(F)$), Z = 1, d_{calcd} = 1.914 g cm^{-3}, μ = 6.07 mm^{-1}, space group $P\bar{1}$, hemisphere data collection in ω at 0.3° scan width in three runs with 606, 435, and 230 frames (ϕ = 0, 88, and 180°) at a detector distance of 4.019 cm (2 θ_{max} = 60°), data reduction with SAINT program (V4.050 Bruker-AXS), empirical absorption correction with redundant data (SADABS program) max/min transmission 0.695/0.524, and R(merg) before/after correction 0.075/0.018; structure solution and refinement on F^2 with SHELXS-96 and SHELXL-93; 8671 intensities read, 6049 unique (R_{int} = 0.0179), and 5676 observed [$I > 2\sigma(I)$], 248 parameters, hydrogen atoms treated as riding groups with a 1.2-fold (1.5-fold for methyl groups) isotropic U value of the equivalent U value of the corresponding C atom. R1 = 0.023; wR2 = 0.072, GooF (F^2) = 0.628, $w^{-1} = \sigma^2(F_o^{\,2}) + (0.1P)^2 + 0.0P$, where $P = [\max(F_o^{\,2}, 0) + 2F_c^{\,2}]/3$, max/min residual electron densities 1.54 and −1.61 eÅ^{-3}.

Results and Discussion

Reaction of phosphaalkene $Me_3SiP{=}C(NMe_2)_2$ (**1**) with an equimolar amount of pivaloyl chloride or benzoyl chloride in *n*-pentane at −30 °C produced the P-acyl phosphaalkenes **2a**,**b** as yellow solids in good yields. Combination of **1** with carbon disulfide or phenyl isothiocyanate under similar conditions afforded the yellow orange P-functionalized phosphaalkenes **2c** and **2d** (Scheme 2).

Several years ago, Markovskii et al. described the reaction between **1** and phenyl isocyanate, which led to an isomeric mixture of insertion products.[14] Replacement of the P-silyl group in **1** ($\delta^{31}P$ = −47.1)[15] by acyl, dithiocarboxy, and thiocarbamoyl functions leads to a significant deshielding of the ^{31}P NMR resonances in **2a**−**d** (δ ^{31}P = 26.4−145). In comparison to this, the

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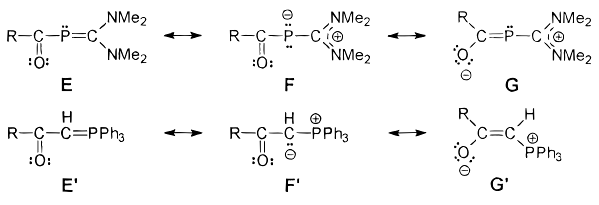
[14] Markovskii, L. N.; Romanenko, V. D.; Pidvarko, T. V. *Zh. Obshch. Khim.* **1983**, *53*, 1672; *Chem. Abstr.* **1983**, *99*, 195100g.

[15] Povolotskii, M. I.; Negrebetskii, V. V.; Romanenko, V. D.; Ivanchenko, V. I.; Sarina, T. V.; Markovskii, L. N. *Zh. Obshch. Khim.* **1990**, *60*, 2238; *Chem. Abstr.* **1991**, *115*, 8934w.

Scheme 3



substitution of the silyl group in $Me_3SiP{=}C(OSiMe_3)$(tBu) (δ $^{31}P = 120$)[16] by the pivaloyl unit to give tBuC(O)P=C($OSiMe_3$)(tBu) (δ $^{31}P = 131$) has much less influence on the ^{31}P NMR resonances.[16] Obviously the electronic structure of the inverse phosphaalkene **1** is much more perturbed by acylation than is observed in the more "classically polarized" phosphaalkenes. This idea is supported by IR evidence. In tBuC(O)P=C($OSiMe_3$)(tBu), an intense band at $v = 1664$ cm^{-1} is assigned to the ν(CO) stretching mode. This value falls in the range of 1630−1690 cm^{-1} usually encountered in acyl phosphanes.[17] In the IR spectra of **2a** and **2b**, strong bands at v 1563 and 1546 cm^{-1}, respectively, indicated a pronounced π-delocalization of electron density onto the carbonyl group. This electronic situation may be described by canonical formulas **E**−**G** similar to the bond description of carbonyl-stabilized ylides (**E′**−**G′**) (Scheme 3).

Consistently, the IR spectra of the ylides Me(O)CCH=PPh_3 and Ph(O)CH=PPh_3 display strong carbonyl bands at v 1540 and 1500 cm^{-1}, respectively.[18]

In the $^{13}C\{^1H\}$ NMR spectra of **2a** and **2b**, doublets at δ 201.4 ($^1J_{PC} = 80.5$ Hz) and 199.3 ($^1J_{PC} = 78.5$ Hz), respectively, are attributed to the tricoodinate carbon atom of the P=C bond. The respective ^{13}C nucleus in **1** gives rise to a doublet at δ 204.0 ($^1J_{PC} = 85.0$ Hz).[15] The carbon atoms of the carbonyl groups in **2a,b** resonate as doublets at δ 231.4 ($^1J_{PC} = 90.8$ Hz) and 215.6 ($^1J_{PC} = 78.7$ Hz), respectively. The ^{13}C NMR resonances due to the P=C and the C=S units in **2c** are registered at δ 193.7 (d, $^1J_{PC} = 87.2$ Hz) and 234.5 (s, br). In keeping with this, the doublet at δ 231.5 ($^1J_{PC} = 72.3$ Hz) in **2d** was assigned to a C=S function and thus may serve as evidence for the presence of a carbamoyl function at the phosphorus atom and disfavor the isomeric thioimidate C(=NPh)$SSiMe_3$ structure.

To substantiate the spectroscopic evidence for a delocalization of negative charge by π-accepting substituents at the phosphorus center, an X-ray structure analysis of **2c** was performed. Single crystals of **2c** were grown from toluene at −30 °C. The results of the structural determination are shown in Figure 1. Selected bond lengths and angles for the molecule are given in Table 1. The analysis confirms the presence of a P-dithiocarboxy-stabilized carbenium phosphanide in which the planar carbenium center C(5) shows multiple bonding to the planarly configurated nitrogen atoms [C(5)−N(1) = 1.341(2) Å; C(5)−N(2) = 1.338(2) Å]. The former PC double bond of the precursor **1** is elongated to a single bond since the P(1)−C(5) distance in **2c** is 1.8264(16) Å [cf. in HP=C(NMe_2)$_2$; d(P=C) = 1.740(1) Å[6]]. Delocalization of negative charge into the C=S bond is obvious by the bond length P(1)−C(4) of 1.7483(16) Å, which is amid the P=C double bond length in nonconjugated phosphaalkenes (1.65−1.67 Å [3]) and the standard value for P−C single bond (1.85 Å). The trigonal-planar carbon atom C(4) (sum of angles 359.88°) is linked to atom S(1) by a single bond of 1.8007(15) Å (sum of single bond covalence radii 1.81 Å) and to S(2) by a double bond of 1.6731(16) Å, which is elongated in comparison to the calculated value for a C=S double bond (1.62 Å [19])

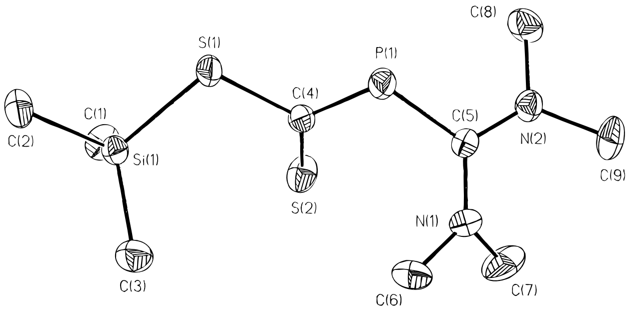


Figure 1. Molecular structure of **2c** in the crystal with ellipsoids drawn in at 50% probability.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 2c

S(1)−C(4)	1.8007(15)	S(1)−Si(1)	2.1732(6)
S(2)−C(4)	1.6731(16)	P(1)−C(4)	1.7483(16)
P(1)−C(5)	1.8264(16)	N(1)−C(5)	1.341(2)
N(1)−C(6)	1.458(2)	N(1)−C(7)	1.464(2)
N(2)−C(5)	1.338(2)	N(2)−C(8)	1.462(2)
N(2)−C(9)	1.466(2)		
C(4)−S(1)−Si(1)	106.08(5)	C(4)−P(1)−C(5)	101.89(7)
C(5)−N(1)−C(6)	122.61(15)	C(5)−N(1)−C(7)	122.24(15)
C(6)−N(1)−C(7)	113.96(16)	C(5)−N(2)−C(8)	122.36(14)
C(5)−N(2)−C(9)	123.29(14)	C(8)−N(2)−C(9)	113.53(14)
S(2)−C(4)−P(1)	130.92(9)	S(2)−C(4)−S(1)	121.43(9)
P(1)−C(4)−S(1)	107.53(8)	N(2)−C(5)−N(1)	118.03(14)
N(2)−C(5)−P(1)	118.87(12)	N(1)−C(5)−P(1)	122.68(12)
Si(1)−S(1)−C(4)−S(2)	29.8		
Si(1)−S(1)−C(4)−P(1)	−153.7		
C(5)−P(1)−C(4)−S(1)	175.9		
C(5)−P(1)−C(4)−S(2)	−8.0		
C(4)−P(1)−C(5)−N(1)	−58.8		
C(4)−P(1)−C(5)−N(2)	128.9		

Such a situation is well-known from the structural data of many β-ketoylides having C=O lengths ranging from 1.22 to 1.30 Å, with most being near 1.25 Å, compared to a determined length of 1.217 Å in a corresponding phosphonium salt. Likewise the C−CO lengths range from 1.35 to 1.48 Å, with most being near 1.40 Å, compared to a determined length of 1.51 Å in a phosphonium salt.[20]

The bond angle C(4)−P(1)-C(5) [101.89(7) Å] is close to the respective value in HP=C(NMe_2)$_2$ [103(1)°].[4] In good agreement with the VSEPR concept, the angle P(1)−C(4)−S(2) of 130.92(9)° clearly exceeds those between the bonds of a lower degree of π-bonding [S(1)−C(4)−S(2) = 121.43(9)°, S(1)−C(4)−P(1) = 107.53(8)°]. The atoms S(1), C(4), S(2), P(1), and C(5) slightly deviate from a planar arrangement as evident from the torsion angles C(5)−P(1)−C(4)−S(1) = 175.9° and C(5)−P(1)−C(4)−S(2) = −8.0°.

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(16) Becker, G. *Z. Anorg. Allg. Chem.* **1977**, *430*, 66.

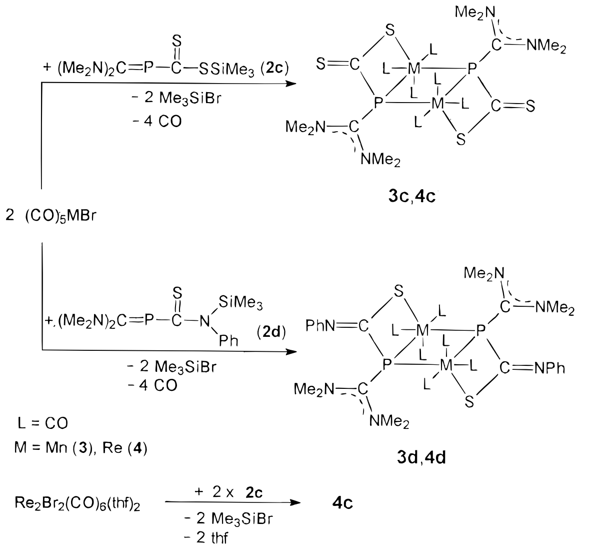
(17) (a) Osaki, T.; Otera, J.; Kawasaki, Y. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 1803. (b) Issleib, K.; Priebe, E. *Chem. Ber.* **1959**, *92*, 3183.

(18) Vicente, J.; Chicote, M. T.; Saura-Llames, I.; Turpin, J.; Fernandez-Baeza, J. *J. Organomet. Chem.* **1987**, *333*, 129.

(19) Shriver, D. F.; Atkins, P. W.; Langford, C. H. *Inorganic Chemistry*, 2 ed.; Oxford University Press: Oxford, 1994; p 58.

(20) *Ylides and Imines of Phosphorus*; Johnson, A. W., Ed.; Wiley: New York, 1993.

Scheme 4



Molecules of the type **2** exhibit a number of donor sites and therefore may act as multidentate ligands in transition metal coordination chemistry.

The phosphaalkenes **2c** and **2d** smoothly reacted with $(CO)_5MBr$ (M = Mn, Re) in toluene (50−80 °C) to afford red (**3c**, **4c**) and orange (**3d**, **4d**) tricyclic complexes in good yield (42.5−82.5%) (Scheme 4).

Complex **4c** was also prepared by the treatment of complex $Re_2(CO)_6Br_2(thf)_2$ with 2 molar equiv of **2c** in a pentane/tetrahydrofuran mixture at ambient temperature (68% yield). The compounds **3c,d** and **4c,d** are air-stable solids which are insoluble in THF, ether, and toluene. They are only slightly soluble in dichloromethane, which hampers the registration of meaningful ^{13}C NMR spectra.

The ν(CO) region in the IR spectra (KBr) of **3c,d** is dominated by two intense bands at ν 1994 and 1908 cm^{-1} (**3c**) and 1998 and 1889 cm^{-1} (**3d**), which points to a facial assembly of three carbonyl ligands in an octahedrally configurated complex. In **4c** and **4d**, more than two ν(CO)bands were observed. The absence of the typical absorptions of the $SiMe_3$ group in the IR and NMR spectra agree with the release of Me_3SiBr during the reaction. Bands of medium intensity at ν 1550 (**4c**) and 1564 and 1550 cm^{-1} (**4d**) are assigned to C═N stretching vibrations. Mass spectra of **4c**,**d** (LSIMS in a nitrobenzyl alcohol matrix) show the peaks of the molecular ions at *m*/*z* 810 (**3d**) and 1073 (**4d**). The ^{31}P-{^1H} NMR spectra of **3c** and **4c** display singlets at δ 121 and 60, which in comparison to the ^{31}P NMR resonance in **2c** (δ 145) are markedly shielded. Similarly, the ^{31}P NMR signals of **3d** (δ −17) and **4d** (δ −116) appear at higher field than in precursor **2d** (δ 82.8).

Constitution and configuration of the novel complexes **3c,d** and **4c,d** were unambiguously manifested by an X-ray diffraction study of **4d**. Crystals of the complex were grown from a saturated solution in hot CH_2Cl_2, which was slowly cooled to ambient temperature. The results of the structural determination are shown in Figure 2. Selected bond lengths and angles for the compound are given in Table 2.

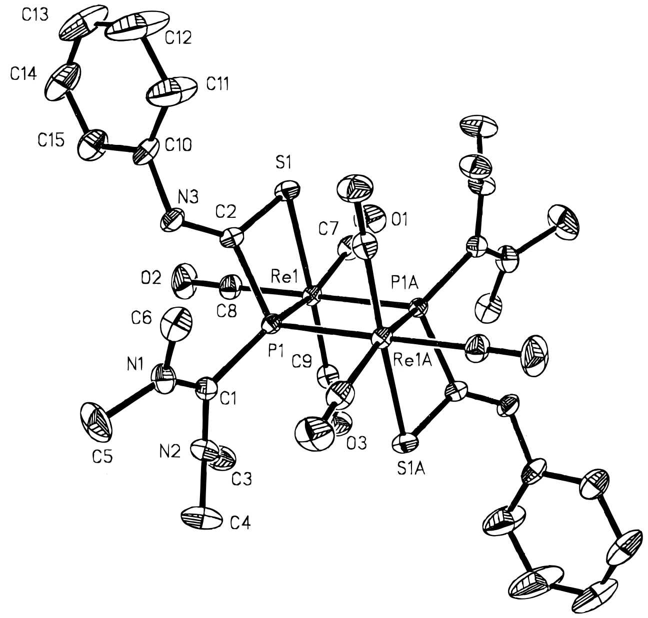


Figure 2. Molecular structure of **4d** in the crystal with ellipsoids drawn in at 50% probability.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 4d

Re(1)−C(9)	1.920(3)	Re(1)−C(7)	1.931(3)
Re(1)−C(8)	1.932(3)	Re(1)−S(1)	2.5198(7)
Re(1)−P(1A)	2.5215(7)	Re(1)−P(1)	2.5292(7)
P(1)−C(2)	1.833(3)	P(1)−C(1)	1.852(3)
P(1)−Re(1A)	2.5215(7)	S(1)−C(2)	1.775(3)
O(1)−C(7)	1.140(4)	O(2)−C(8)	1.155(4)
O(3)−C(9)	1.155(4)	N(1)−C(1)	1.338(4)
N(1)−C(6)	1.465(4)	N(1)−C(5)	1.470(4)
N(2)−C(1)	1.336(4)	N(2)−C(3)	1.463(4)
N(2)−C(4)	1.478(4)	N(3)−C(2)	1.275(3)
N(3)−C(10)	1.416(4)		
C(9)−Re(1)−C(7)	93.63(12)	C(9)−Re(1)−C(8)	92.60(13)
C(7)−Re(1)−C(8)	88.87(13)	C(9)−Re(1)−S(1)	173.19(9)
C(7)−Re(1)−S(1)	92.98(9)	C(8)−Re(1)−S(1)	89.15(10)
C(9)−Re(1)−P(1A)	89.92(9)	C(7)−Re(1)−P(1A)	96.44(9)
C(8)−Re(1)−P(1A)	173.97(9)	S(1)−Re(1)−P(1A)	87.73(2)
C(9)−Re(1)−P(1)	105.27(9)	C(7)−Re(1)−P(1)	159.05(9)
C(8)−Re(1)−P(1)	99.02(10)	S(1)−Re(1)−P(1)	67.94(2)
P(1A)−Re(1)−P(1)	75.02(2)	C(2)−P(1)−C(1)	108.40(12)
C(2)−P(1)−Re(1A)	115.02(9)	C(1)−P(1)−Re(1A)	106.87(8)
C(2)−P(1)−Re(1)	87.85(8)	C(1)−P(1)−Re(1)	132.98(9)
Re(1A)−P(1)−Re(1)	104.98(2)	C(2)−S(1)−Re(1)	89.42(9)
C(1)−N(1)−C(6)	125.0(3)	C(1)−N(1)−C(5)	121.3(3)
C(6)−N(1)−C(5)	113.6(3)	C(1)−N(2)−C(3)	123.9(3)
C(1)−N(2)−C(4)	121.1(3)	C(3)−N(2)−C(4)	113.7(3)
C(2)−N(3)−C(10)	119.6(3)	N(2)−C(1)−N(1)	118.4(3)
N(2)−C(1)−P(1)	118.8(2)	N(1)−C(1)−P(1)	122.4(2)
N(3)−C(2)−S(1)	129.9(2)	N(3)−C(2)−P(1)	127.0(2)
S(1)−C(2)−P(1)	102.86(13)	O(1)−C(7)−Re(1)	177.2(3)
O(2)−C(8)−Re(1)	176.8(3)	O(3)−C(9)−Re(1)	179.5(3)

The analysis of **4d** reveals a centrosymmetrical tricyclic molecule with an anti orientation of the two phenyl isothiocyanate units, which are connected to the central planar ring by their carbon and sulfur atoms. The central ring is a trapezium with Re−P bond lengths of 2.5292(7) Å [Re(1)−P(1)] and 2.5215(7) Å [Re(1)−P(1A)]. These values compare well with the Re−P distances in $Re_2Br_2(CO)_6(P_2Ph_4)$ [2.508(5) Å].[21] A summary of 10 independent Re−P bond lengths in univalent rhenium complexes range from 2.413(4) to 2.538(5) Å (av = 2.461 Å).[21] The endocyclic angle at phosphorus in central ring Re(1)−P(1)−Re(1A) [104.98(2)°] is more

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[21] Atwood, J. L.; Newell, J. K.; Hunter W. E.; Bernal, I.; Calderazzo, F.; Mavani, I. P.; Vitali, D. *J. Chem. Soc., Dalton Trans.* **1978**, 1189.

obtuse than that at the rhenium atoms [P(1)−Re(1)−P(1A) = 72.02(2)°]. The four-membered ring defined by the atoms Re(1), P(1), C(2), and S(1) is puckered with an interplanar angle of 37.0° between the triangular planes Re(1), P(1), S(1) and P(1), C(2), S(1). The plane defined by the heavy atoms S(1), Re(1), and P(1) and the central ring enclose a dihedral angle of 86.3°. The trigonal planar carbon atom C(2) is linked to the exocyclic phenylimino group by a CN double bond of 1.275(3) Å. The remaining atoms S(1) and P(1) are ligated to C(2) by single bonds of 1.775(3) Å [S(1)−C(2)] and 1.833(3) Å [P(1)−C(2)]. The interatomic distance Re(1)−S(1) [2.5198(7) Å] exceeds that of the rhenium−sulfur single bonds in $Re_2Br_2(CO)_6(S_2Ph_2)$ (2.487 Å)[22] and $Re_2Br_2(CO)_6(S_2Me_2)$ (2.486 Å).[23] The phosphorus atoms are tetracoordinate featuring exocyclic PC single bonds of 1.852(3) Å to the planar carbon atom C(1) of a bis(dimethylamino)carbenium unit. The plane defined by the atoms N(1), C(1), and N(2) is orientated nearly orthogonally to the central Re_2P_2 ring, featuring a dihedral angle of 100.3°. The rhenium atoms are centered in a distorded octahedron with a facial arrangement of the three carbonyl ligands. The rhenium carbon bond lengths range from 1.920(3) to 1.932(3) Å and thus within experimental error are comparable to the respective data in $Re_2Br_2(CO)_6(E_2R_2)$ [E_2R_2 = S_2Ph_2 (1.89 Å),[22] S_2Me_2 (1.87 Å),[23] and P_2Ph_4 (1.90 Å).[21] The 12 bond angles about the rhenium atom range from 67.94(2)° [S(1)−Re(1)−P(1)] to 105.27(9)° [C(9)−Re(1)−P(1)]. The organophosphorus building block in the complex can be characterized as an η^2(P,S)−μ(P) ligand, thus constituting a novel mode of coordination in phosphaalkene chemistry.

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Supporting Information Available: Tables of X-ray data, atomic coordinates, thermal parameters, and complete bond distances and angles and thermal ellipsoid plots for compounds **2c** and **4d** as well as ^1H and $^{13}C\{^1H\}$NMR spectra of **2a** and **2b** (19 pages). Ordering information is given on any current masthead page.

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(22) Bernal, I.; Atwood, J. L.; Calderazzo, F.; Vitali, D. *Gazz. Chem. Ital.* **1976**, *106*, 971.

(23) Bernal, I.; Atwood, J. L.; Calderazzo, F.; Vitali, D. *Isr. J. Chem.* **1976/77**, *15*, 153.