Conversion of CS_2 to Thioaldehyde at a Single Iron Center

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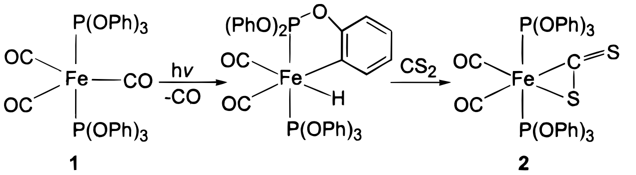
Summary: UV-irradiation of the thiocarbonyl complex $Fe(CO)_2(CS)\{P(OPh)_3\}_2$, prepared from $Fe(CO)_2(CS_2)\{P(OPh)_3\}_2$, affords the unstable thioaldehyde complex $Fe(CO)_2\{P(OPh)_3\}\{(PhO)_2P(OC_6H_4)C(H)S\}$, which reacts with $P(OPh)_3$ to give $Fe(CO)\{P(OPh)_3\}_2\{(PhO)_2P(OC_6H_4)C(H)S\}$, the crystal structure of which reveals an η^2(C,S)-bonded thioaldehyde group formally derived from insertion of the thiocarbonyl C atom into an ortho C−H bond of an axially bound $P(OPh)_3$ phenyl group.

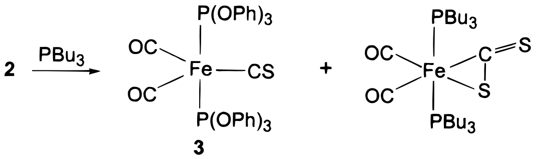
Transition metal complexes containing sulfur are of interest both as potential analogues of intermediates involved in catalytic CO/H_2 chemistry[1] and because sulfur is a potent poison of many of these catalytic systems.[2] Metal-mediated reduction of CS_2 to H_2CS has been demonstrated in only a few cases,[3] and examples of reduction with concomitant C−C bond formation are also rare.[4] In this preliminary communication we report the stepwise conversion of CS_2 to thioaldehyde at a metal center.

Photolysis of the tricarbonyl complex $Fe(CO)_3\{P(OPh)_3\}_2$ (**1**) to give the orthometalated iron-hydride derivative $HFe(CO)_2\{P(OPh)_3\}\{(PhO)_2P(OC_6H_4)\}$ and subsequent reaction with CS_2 is one[5a] of a number of routes to $Fe(CO)_2(\eta^2\text{-}CS_2)\{P(OPh)_3\}_2$ (**2**)[5] (Scheme 1). Solutions of **2** in acetonitrile or similar donor solvents have been shown to react with PBu_3 to afford the thiocarbonyl derivative $Fe(CO)_2(CS)\{P(OPh)_3\}_2$ (**3**) (ca. 85%) by sulfur abstraction and $Fe(CO)_2(\eta^2\text{-}CS_2)(PBu_3)_2$ (ca. 15%) by ligand exchange (Scheme 2).[6] In view of the preferential labilization of CO compared to CS upon UV-irradiation,[7] it was anticipated that photolysis of **3** would follow the same course as that of **1**, i.e. loss of CO and orthometalation to afford $HFe(CO)(CS)\{P(OPh)_3\}\{(PhO)_2P(OC_6H_4)\}$. Instead the reaction proceeded with retention of both CO ligands (ν_{CO} 2014 and 1955 cm^{-1} vs 1995 and 1936 cm^{-1} in **3**) and the disappearance of the strong CS absorption band at 1266 cm^{-1}. A single reaction product, **4**, was isolated as an orange-brown oily solid.[8] Slow crystallization of **4**, however, afforded in low yield yellow crystals of a new compound, **5**, which exhibited only one ν(CO) absorption band at 1951 cm^{-1} in the IR spectrum. This compound was analyzed by X-ray diffraction, and its molecular structure is shown in Figure 1.[9]

Scheme 1



Scheme 2



It reveals that **5** contains a bidentate ligand comprising a thioaldehyde moiety RCHS formally derived from insertion of the thiocarbonyl C atom of **3** into an ortho C−H bond of an axially bound $P(OPh)_3$ phenyl group. The CS of the thioaldehyde group is bonded to the Fe center in the η^2(C,S) coordination mode and is essentially coplanar with the CO group and the phosphorus atom of a second $P(OPh)_3$ ligand. The remaining

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(8) Synthesis of **4**: A stirred solution of **3** (500 mg, 0.64 mmol) in toluene (50 mL) was cooled in an ice−water bath and irradiated with a 125 W mercury-vapor lamp until the starting material was consumed (typically 2−3 h) as determined by IR spectroscopy. The solvent volume was reduced, and the residue was chromatographed on alumina (30 × 2.5 cm). An orange-brown band was eluted with toluene and concentrated to afford **4** as an oily solid (304 mg).

(9) Single crystals of **5** were obtained from acetonitrile solution. Crystallographic data: Chemical formula $C_{56}H_{45}FeO_{10}P_3S$, molecular weight 1058.74, triclinic, space group $P\bar{1}$ (No. 2), $a = 11.3305(15)$ Å, $b = 12.1012(19)$ Å, $c = 20.204(3)$ Å, $\alpha = 102.365(14)°$, $\beta = 94.862(16)°$, $\gamma = 107.524(10)°$, $V = 2547.1(6)$ Å^3, $Z = 2$, $T = 290$ K, density = 1.38 g cm^{-3}, $F(000) = 1096$, $\mu = 4.91$ cm^{-1}, 9439 reflections from 2 to 25.5°, 5274 unique (with $I > 2\sigma I$), R-factor is 0.0546, GoF = 0.93, $wR_2 = 0.117$ (based on F^2 for all reflections), final Δ-map is −0.32 to +0.30 e Å^{-3}.

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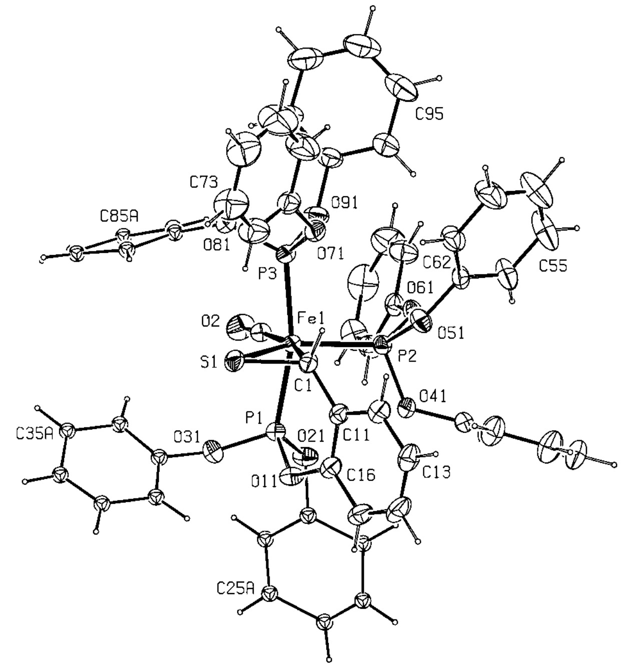


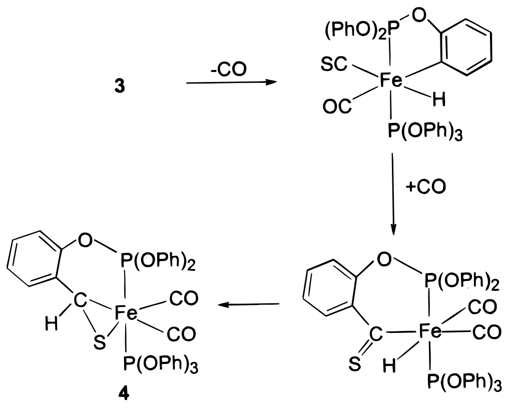
Figure 1. Molecular structure of **5**. Selected bond lengths (Å) and angles (deg): Fe1−P1, 2.1468(11); Fe1−P2, 2.1255(11); Fe1−P3, 2.1696(11); Fe1−S1, 2.2760(11); Fe1−C1, 2.076(4); Fe1−C2, 1.758(4); S1−C1, 1.752(4); O2−C2, 1.161(4); C1−C11, 1.470(5); C1−H1, 0.95(3); P1−Fe1−P3, 165.70(4); P2−Fe1−C1, 87.48(10); P2−Fe1−C2, 106.61(12); S1−Fe1−C1, 47.21(10); S1−Fe1−C2, 118.50(12); S1−C1−H1, 112.1(17); C11−C1−H1, 111.5(17).

coordination site is occupied by a third $P(OPh)_3$ ligand such that the overall geometry about the metal center may be described as distorted trigonal bipyramidal.

Although the $P(OPh)_2\{OC_6H_4C(H)S\}$ ligand has not previously been reported, mononuclear compounds containing η^2-thioaldehydes RCHS have been structurally characterized for R = H,[10] Me,[11] and Ph.[12] As observed in the complexes of these thioaldehydes,[10−12] the CS bond length of 1.752(4) Å in **5** is intermediate between that of a typical C−S single bond (1.80−1.82 Å) and that found for the C═S double bond in organic thiocarbonyls (ca. 1.60 Å).[13]

The solution-state spectroscopic data for **5**[14] are in accordance with the solid-state structure. The η^2(C,S) coordination mode is confirmed by the high-field shifts of both the ^1H and the ^{13}C NMR signals of the CHS group (δ 4.73 and 50.0, respectively); in η^1(S)-coordinated thioaldehyde ligands the ^{13}C NMR signals are substantially deshielded at ca. δ 200.[15] The strongly trans-coupled nuclei P1 and P3 appear as the AB portion of an ABX spin system in the $^{31}P\{^1H\}$ NMR spectrum. The signal at δ 140.2 is assigned to P1 in view of the expected shift to higher field for ^{31}P in a six-membered chelate ring.[16] A doublet of doublets at δ 165.9 exhibiting small cis couplings is assigned to P2.

Scheme 3



Since **5** may also be obtained in good yield[17] by refluxing solutions of **4** with $P(OPh)_3$, we propose that **4** is the dicarbonyl intermediate $Fe(CO)_2\{P(OPh)_3\}\{(PhO)_2P(OC_6H_4)C(H)S\}$[18] and suggest Scheme 3 to account for its formation. The first step in this mechanism is analogous to the established reactivity of the tricarbonyl complex **1** on UV-irradiation (see above), and the subsequent steps have precedent in the work of Roper et al., who have demonstrated the particular facility with which CS undergoes migratory-insertion reactions.[19] In the absence of added phosphite, slow decomposition of **4** affords free $P(OPh)_3$, which converts the remaining **4** to **5**: the $^{31}P\{^1H\}$ NMR spectrum of a freshly prepared sample of **4** exhibits an AB pattern ($^2J_{PP}$ = 455 Hz) the intensity of which decreases over a period of days with the formation of free $P(OPh)_3$ (δ 128.8) and the appearance of resonances attributable to **5**. When the photolysis of the thiocarbonyl **3** is repeated in the presence of $P(OPh)_3$, then **5** is formed exclusively.

Whereas **4** reacts with added $P(OPh)_3$ to substitute CO (Scheme 4), in the presence of the strong donor ligand PMe_3, **4** undergoes rapid substitution of $P(OPh)_3$ to afford the dicarbonyl $Fe(CO)_2(PMe_3)\{(PhO)_2P(OC_6H_4)C(H)S\}$ (**6**).[20] This reactivity presumably derives from

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(10) $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}H_2C{=}S)][PF_6]$, d(C−S) = 1.742(9) Å: Buhro, W. E.; Etter, M. C.; Georgiou, S.; Gladysz, J. A.; McCormick, F. B. *Organometallics* **1987**, *6*, 1150. $(\eta^5\text{-}C_5H_5)_2Ti(\eta^2\text{-}H_2C{=}S)(PMe_3)$, d(C−S) = 1.744(3) Å: Park, J. W.; Henling, L. M.; Schaefer, W. P.; Grubbs, R. H. *Organometallics* **1990**, *9*, 1650.

(11) $(\eta^5\text{-}C_5H_5)_2Zr\{\eta^2\text{-}MeC(H){=}S\}(PMe_3)$, d(C−S) = 1.785(11) Å, 1.739(13) Å: Buchwald, S. L.; Nielsen, R. B.; Dewan, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 1590.

(12) $(Et_2NCS_2)(Et_2NCS)W(CO)\{\eta^2\text{-}PhC(H){=}S\}$: Mayr, A.; McDermott, G. A.; Dorries, A. M.; Holder, A. K.; Fultz, W. C.; Rheingold, A. L. *J. Am. Chem. Soc.* **1986**, *108*, 310. $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)\{\eta^2\text{-}PhC(H){=}S\}][PF_6]$, d(C−S) = 1.70(1) Å: Schenk, W. A.; Burzlaff, N.; Burzlaff, H. *Z. Naturforsch.* **1994**, *49b*, 1633.

(13) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. In *Structure Correlation, Vol. 2*; Bürgi, H.-B., Dunitz, J. D., Eds.; VCH Publ.: Weinheim, Germany, 1994.

(14) Mp 147 °C (dec). Anal. Calcd for $C_{56}H_{45}FeO_{10}P_3S$: C, 63.52; H, 4.28; S, 3.03. Found: C, 63.32; H, 4.42; S, 3.17. IR (KBr) ν(CO) 1951 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) 7.70−6.52 (m, 44H, Ph), 4.73 (m, 1H, C*H*S); $^{13}C\{^1H\}$ NMR (67.9 MHz, $CDCl_3$) 211.5 (m, *C*O), 153.2−120.5 (Ph), 50.0 (m, *C*HS); $^{31}P\{^1H\}$ NMR (109 MHz, $CDCl_3$) 165.9 (dd, $^2J_{PP}$ = 97.7, 82.4 Hz, P2), 151.9 (dd, $^2J_{P3P1}$ = 450.0 Hz, $^2J_{P3P2}$ = 82.4 Hz, P3), 140.2 (dd, $^2J_{P1P3}$ = 450.0 Hz, $^2J_{P1P2}$ = 97.7 Hz, P1).

(15) Schenk, W. A.; Stur, T.; Dombrowski, E. *Inorg. Chem.* **1992**, *31*, 723. Schenk, W. A.; Stur, T.; Dombrowski, E. *J. Organomet. Chem.* **1994**, *472*, 257.

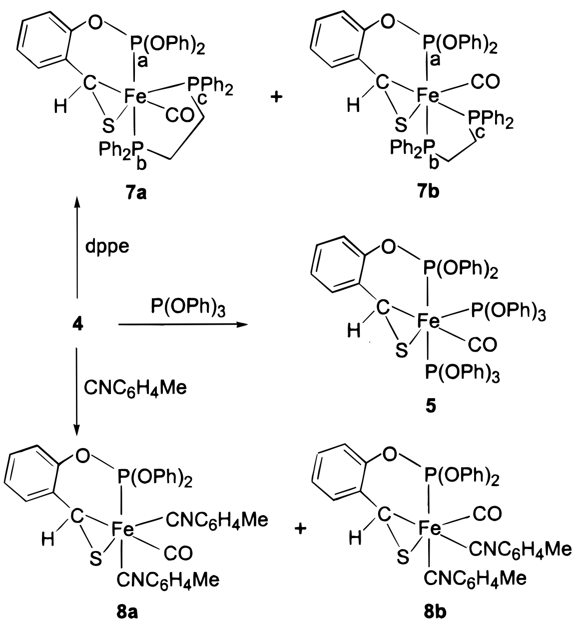
(16) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

(17) A solution of **3** (825 mg, 1.06 mmol) in toluene (50 mL) was photolyzed as described in ref 8. A 2-fold excess of the ligand $P(OPh)_3$ was then added, and the mixture was heated to reflux for 3 h. The solvent volume was reduced and the residue chromatographed on alumina (30 × 2.5 cm). A bright yellow band was eluted with toluene; recrystallization from toluene/hexane afforded **5** (586 mg, 52%).

(18) IR (CH_2Cl_2) ν(CO) 2014 (s), 1955 (vs) cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) 7.71−6.50 (m, 29H, Ph), 4.87 (dd, 1H, $^3J_{HP}$ = 6.1, 3.8 Hz, C*H*S); $^{13}C\{^1H\}$ NMR (67.9 MHz, $CDCl_3$) 212.6 (3-line pattern, J = 29.0 Hz, *C*O), 210.2 (dd, $^2J_{CP}$ = 45.2, 40.1 Hz, *C*O), 153.6−120.0 (Ph), 52.7 (3-line pattern, J = 11.1 Hz, *C*HS); $^{31}P\{^1H\}$ NMR (109 MHz, $CDCl_3$) 158.3 (d, $^2J_{PP}$ = 454.7 Hz, P), 148.2 (d, $^2J_{PP}$ = 454.7 Hz, P-thioaldehyde).

(19) Clark, G. R.; Collins, T. J.; Hall, D.; James, S. M.; Roper, W. R. *J. Organomet. Chem.* **1977**, *141*, C5. Clark, G. R.; Collins, T. J.; Marsden, K.; Roper, W. R. *J. Organomet. Chem.* **1983**, *259*, 215.

Scheme 4



the strongly electron-withdrawing nature of the η^2-thioaldehyde ligand (reflected in the length of the CS bond in **5**) and consequent electron deficiency of the metal center {evidenced by the high ν(CO) frequencies of both **4** and **5**}. Treatment of **4** with 1,2-bis(diphenylphosphino)ethane (dppe) affords the complex Fe(CO)(η^2-dppe){(PhO)$_2$P(OC$_6$H$_4$)C(H)S} (**7**)[21] as a 9:1 mixture of isomers (Scheme 4). By analogy with the structure of **5** we propose **7a** as the major isomer. The reaction of **4** with *p*-tolylisocyanide similarly affords a mixture of isomers Fe(CO)(*p*-CNC$_6$H$_4$Me)$_2${(PhO)$_2$P(OC$_6$H$_4$)C(H)S} (**8**)[22] (Scheme 4) but in approximately 4:3 ratio.

In summary, this work describes a facile two-step conversion of coordinated CS$_2$ via CS to an unusual bidentate thioaldehyde ligand and provides a contrast of the reactivity of the thiocarbonyl complex Fe(CO)$_2$(CS){P(OPh)$_3$}$_2$ with that of its oxygenate analogue Fe(CO)$_3${P(OPh)$_3$}$_2$. Further efforts are directed at exploring the scope of these reactions.

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Supporting Information Available: Tables of crystallographic data for **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[20] Compound **6** was prepared analogously to **5** by 30 min reflux of **4** with excess PMe$_3$. Yield 40%. Mp 124 °C. Anal. Calcd for C$_{24}$H$_{24}$FeO$_5$P$_2$S: C, 53.19; H, 4.46; S, 5.92. Found: C, 53.23; H, 4.52; S, 6.31. IR (KBr) ν(CO) 1990 (s), 1924 (vs) cm^{-1}. ^{1}H NMR (270 MHz, CDCl$_3$) 7.41−6.62 (m, 14H, Ph), 4.09 (dd, 1H, $^3J_{HP} = 5.9, 3.7$ Hz, C*H*S), 1.20 (dd, 9H, $^2J_{HP} = 9.3$ Hz, $^4J_{HP} = 2.0$ Hz, C*H*$_3$); ^{13}C{^{1}H} NMR (67.9 MHz, CDCl$_3$) 214.2 (3-line pattern, $J = 25.6$ Hz, *C*O), 212.5 (dd, $^2J_{CP} = 37.5, 30.7$ Hz, *C*O), 152.1−120.4 (Ph), 50.8 (dd, $^2J_{CP} = 12.0, 6.9$ Hz, *C*HS), 15.4 (d, $^1J_{CP} = 30.7$ Hz, *C*H$_3$); ^{31}P{^{1}H} NMR (109 MHz, CDCl$_3$) 166.0 (d, $^2J_{PP} = 283.8$ Hz, phosphite), 21.3 (d, $^2J_{PP} = 283.8$ Hz, phosphine).

[21] Compound **7** was prepared analogously to **5** by 1 h reflux of **4** with excess dppe. Yield 51%. Mp 214 °C (dec). Anal. Calcd for C$_{46}$H$_{39}$FeO$_4$P$_3$S: C, 66.08; H, 4.70; S, 3.83. Found: C, 66.32; H, 4.61; S, 4.10. IR (KBr) ν(CO) 1914 (m), 1896 (vs) cm^{-1}. ^{1}H NMR (270 MHz, CDCl$_3$) 7.94−6.43 (m, 34H, Ph), 3.87 (br m, 1H, C*H*S), 2.90 (br d, 1H, $J = 18$ Hz, C*H*), 2.68 (br d, 1H, $J = 18$ Hz, C*H*), 2.36 (br s, 1H, C*H*), 2.10 (br s, 1H, C*H*); ^{13}C{^{1}H} NMR (67.9 MHz, CDCl$_3$) only major isomer detected, 216.0 (m, *C*O), 153.0−119.7 (Ph), 46.3 (m, *C*HS), 32.7 (ddd, $^1J_{CP} = 27.1$ Hz, $^2J_{CP} = 16.9$ Hz, $^3J_{CP} = 6.7$ Hz, *C*H$_2$), 28.0 (dd, $^1J_{CP} = 26.3$ Hz, $^2J_{CP} = 18.8$ Hz, *C*H$_2$); ^{31}P{^{1}H} NMR (109 MHz, CDCl$_3$) major isomer, 158.3 (dd, $^2J_{PaPb} = 289.9$ Hz, $^2J_{PaPc} = 73.3$ Hz, P$_a$), 87.4 (dd, $^2J_{PbPa} = 289.9$ Hz, $^2J_{PbPc} = 27.5$ Hz, P$_b$), 81.2 (dd, $^2J_{PcPb} = 73.2$ Hz, $^2J_{PcPa} = 27.5$ Hz, P$_c$); minor isomer, 163.3 (dd, $^2J_{PaPb} = 274.7$ Hz, $^2J_{PaPc} = 69.5$ Hz, P$_a$), 89.6 (dd, $^2J_{PcPa} = 69.5$ Hz, $^2J_{PcPb} = 28.3$ Hz, P$_c$), 74.9 (dd, $^2J_{PbPa} = 274.7$ Hz, $^2J_{PbPc} = 28.3$ Hz, P$_b$).

[22] Compound **8** was prepared analogously to **5** by 2 h reflux of **4** with excess *p*-CNC$_6$H$_4$Me. Yield 18%. Mp 133−134 °C (dec). Anal. Calcd for C$_{36}$H$_{29}$FeN$_2$O$_4$PS: C, 64.29; H, 4.35; N, 4.17; S, 4.77. Found: C, 63.93; H, 4.45; N, 3.90; S, 4.94. IR (KBr) ν(CN) 2144 (s), 2096 (vs); ν(CO) 1948 (br vs) cm^{-1}. ^{1}H NMR (270 MHz, CDCl$_3$) major isomer, 7.58−6.61 (m, Ph), 4.80 (d, 1H, $^3J_{HP} = 3.1$ Hz, C*H*S), 2.40 (s, 3H, C*H*$_3$), 2.35 (s, 3H, C*H*$_3$); minor isomer, 7.58−6.61 (m, Ph), 4.88 (d, 1H, $^3J_{HP} = 3.7$ Hz, C*H*S), 2.34 (s, 3H, C*H*$_3$), 2.28 (s, 3H, C*H*$_3$); ^{13}C{^{1}H} NMR (67.9 MHz, CDCl$_3$) major isomer, 213.1 (d, $^2J_{CP} = 40.9$ Hz, *C*O), *C*N not detected, 152.2−117.2 (Ph), 48.0 (d, $^2J_{CP} = 11.9$ Hz, *C*HS), 21.6 (br s, 2 H *C*H$_3$); minor isomer, 214.8 (d, $^2J_{CP} = 35.8$ Hz, *C*O), *C*N not detected, 152.2−117.2 (Ph), 49.4 (d, $^2J_{CP} = 11.9$ Hz, *C*HS), 21.5 (br s, 2H *C*H$_3$); ^{31}P{^{1}H} NMR (109 MHz, CDCl$_3$) major isomer, 162.5 (s); minor isomer, 165.2 (s).