Organometallics 1988, 7, 978-983

Transition-Metal-Substituted Diphosphenes. 12.[1] Transition-Metal Sulfur Ylide Complexes. 25.[2] Alkylidene Transfer to the P=P Double Bond of Diphosphenyl Complexes by Means of the Sulfur Ylides $(CH_3)_2S(O)=CH_2$ and $(c\text{-}C_3H_4)SPh_2$. X-ray Structure Analysis of $(\eta^5\text{-}C_5Me_5)(CO)_2Fe\overline{PC(CH_2CH_2)P}Ar$ (Ar = 2,4,6-t-$Bu_3C_6H_2$)

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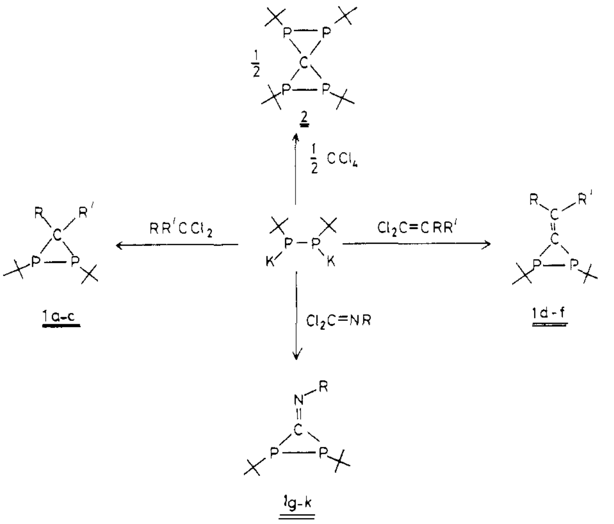
Received October 22, 1987

The reaction of $[(\eta^5\text{-}C_5Me_5)(CO)_2MP{=}PAr]$ (M = Fe, Ru; Ar = 2,4,6-t-$Bu_3C_6H_2$) with $(CH_3)_2S(O){=}CH_2$ in THF at 20 °C afforded the transition-metal-functionalized diphosphiranes $(\eta^5\text{-}C_5Me_5)(CO)_2M\overline{PCH_2P}Ar$ as orange-yellow solids. Similarily the first 1,2-diphosphaspiro[2.2]pentanes were synthesized from $(\eta^5\text{-}C_5Me_5)(CO)_2MP{=}PAr$ and diphenylsulfonium cyclopropanide. The novel compounds were characterized by elemental anaylses and spectroscopic methods (IR, ^1H, ^{13}C, and ^{31}P NMR, and mass spectroscopy). The molecular structure of the 1,2-diphosphaspiro[2.2]pentane $(\eta^5\text{-}C_5Me_5)(CO)_2Fe\overline{PC(CH_2CH_2)P}Ar$ was established by a complete single-crystal differaction study [$P\bar{1}$ space group; $Z = 2$, $a = 8.344$ (3) Å, $b = 10.772$ (4) Å, $c = 19.005$ (8) Å, $\alpha = 92.79$ (3)°, $\beta = 91.04$ (3)°, $\gamma = 93.69$ (3)°].

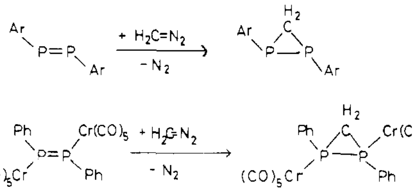
There are several synthetic pathways to diphosphiranes described in the literature. First of all worth mentioning is the pioneering work of Baudler utilizing a cyclocondensation reaction between dimetalated diphosphines and geminal alkyl dichlorides,[3] 1,1-dichloroalkenes,[3,4] and isocyanide dichlorides.[5] The employment of carbon tetrachloride leads to a first tetraphosphaspiro[2.2]pentane derivative[6] (eq 1).



(1)

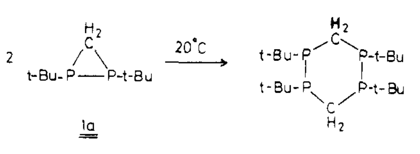
a, R = H, R′ = H; **b**, R = H, R′ = Me; **c**, R = Me, R′ = Me; **d**, R = H, R′ = H; **e**, R = Me, R′ = Me; **f**, R = 4-ClC_6H_4, R′ = 4-ClC_6H_4; **g**, R = 2,4-t-$Bu_2C_6H_2$; **h**, R = 2-t-BuC_6H_4; **i**, R = 2,4,6-$Me_3C_6H_2$; **j**, R = 2-MeC_6H_4; **k**, R = 4-Cl-2-Me-C_6H_3

Another approach to these heterocycles is based upon the treatment of diphosphenes[7] and their transition-metal complexes[8] with diazoalkanes (eq 2). Moreover the reaction of $P(NMe_2)_3$, PCl_3, and $AlCl_3$ led to cations with a P_2C ring skeleton.[9] As pointed out by Baudler the thermal stability of diphosphiranes is highly dependent on the steric requirements of the ligands present. Thus the methylene derivative **1a** easily dimerizes to six-membered cyclodicarbaphosphane (eq 3), whereas the propylidene compound **1b** can be heated for a short time up to 200 °C without decomposition.



(2a)

(2b)



(3)

In the course of our investigations of transition-metal-substituted diphosphenes (diphosphenyl complexes), we studied the chemical behavior of such compounds toward sulfur ylides which are known as excellent cyclopropanating reagents in organic chemistry.[10] Part of our results have been reported in a preliminary communication.[2]

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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 in C_6D_6 solution at ambient temperature. Electron-impact mass spectra were recorded on a Varian MAT 312 spectrometer.

Materials. The diphosphenyl complexes (η^5-C_5Me_5)(CO)$_2$MP=PAr (M = Fe, Ru; Ar = 2,4,6-*t*-$Bu_3C_6H_2$),[11] a THF solution of the sulfur ylide $Me_2S(O){=}CH_2$,[12] the salt [c-$C_3H_5SPh_2$]BF_4,[13] and an etheral solution of diazomethane[14] were prepared as described in the literature. KO-*t*-Bu was purchased commercially. All solvents were rigorously dried with an appropriate drying agent and distilled before use. Silica gel 60 (70–230 mesh, ASTM, Merck) was used for column chomatography.

Preparation of Compounds. (η^5-C_5Me_5)(CO)$_2$FePCH$_2$PAr (4a) (Path a). To a solution of 2.02 g (3.64 mmol) of (η^5-C_5Me_5)(CO)$_2$FeP=PAr (**3a**) in 20 mL of THF was added 43.7 mL of a 0.5 M solution of $Me_2S(O){=}CH_2$ in THF (21.85 mmol) at 20 °C and the mixture stirred for 4 h. Solvent was removed in vacuo, and the dark brown residue was chromatographed on silica gel. Development with petroleum ether at −30 °C gave two yellow bands. From the second yellow band 0.93 g (45%) of orange dicarbonyl(pentamethylcyclopentadienyl)[2-(2,4,6-tri-*tert*-butylphenyl)diphosphiranido(1−)]iron (**4a**) was isolated: mp 188 °C; IR (cyclopentane) 1996 (vs), 1949 (vs) cm^{-1} (ν(CO)); ^{1}H NMR δ 1.25 (s, 9 H, *p*-*t*-Bu), 1.38 (s, 15 H, $C_5(CH_3)_5$), 1.70 (m, 1 H, H_A), 1.88 (s, 18 H, *o*-*t*-Bu), 2.06 (m, 1 H, H_B), 7.38 (d, $^4J_{PH}$ = 1.8 Hz, 2 H, *m*-phenyl H); ^{13}C{^{1}H}NMR δ 9.20 (d, $^3J_{PC}$ = 7.1 Hz, $C_5(CH_3)_5$), 23.03 (dd, $^1J_{PC}$ = 48.6, 60.2 Hz, CH_2), 31.44 (s, *p*-$C(CH_3)_3$), 34.33 (d, J_{PC} = 2.6 Hz), and 34.53 (d, J_{PC} = 2.9 Hz, *o*-$C(CH_3)_3$), 34.50 (s, *p*-$C(CH_3)_3$), 39.62 (s, *o*-$C(CH_3)_3$), 95.78 (s, $C_5(CH_3)_5$), 122.64 (s), 147.33 (s), 156.64 (d, J_{PC} = 2.6 Hz, aryl C), 216.6 (s, FeCO), 217.4 (d, $^2J_{PC}$ = 24 Hz, FeCO); ^{31}P{^{1}H} NMR δ −91.70 (d, $|^1J_{PP}|$ = 170,9 Hz, PFe), −177.47 (d, $|^1J_{PP}|$ = 170.9 Hz, P aryl); MS/EI (70 eV, 70 °C), *m/e* 598 (M$^+$). Anal. Calcd for $C_{31}H_{46}FeO_2P_2$ (568.5): C, 65.49; H, 8.16; Fe, 9.82. Found: C, 65.34; H, 8.20; Fe, 9.97.

Path b. A solution of 2.27 g (4.09 mmol) of **3a** in 30 mL of THF was treated dropwise with 24.5 mL of a 1 M diazomethane solution in ether (vivid effervescence). After 2 h of stirring at 20 °C all volatiles were removed in vacuo. Workup as described above yielded 0.89 g of orange **4a** (38%).

(η^5-C_5Me_5)(CO)$_2$RuPCH$_2$PAr (4b) (Path a). Analogously the reaction of 1.22 g (2.02 mmol) of (η^5-C_5Me_5)(CO)$_2$Ru-P=P-Ar (**3b**) with 10 mmol of $Me_2S(O){=}CH_2$ in 30 mL of THF yielded 0.417 g (32%) of yellow dicarbonyl(pentamethylcyclopentadienyl) [2-(2,4,6-tri-*tert*-butylphenyl)diphosphiranido(1−)]ruthenium (**4b**): mp 170 °C; IR (cyclopentane) 2016 (vs), 1959 (vs) cm^{-1} (ν(CO)); ^{1}H NMR δ 1.25 (s, *p*-*t*-Bu), 1.51 (s, $C_5(CH_3)_5$), 1.78 (dd, $^2J_{H_AH_B}$ = 8.8 Hz, $^2J_{P^1H_A}$ = 24.9 Hz, 1 H, H_A), 1.89 (s, *o*-*t*-Bu), 2.26 (dd, $^2J_{H_AH_B}$ = 8.8 Hz, $^2J_{P^2H_B}$ = 21.8 Hz, 1 H, H_B), 7.38 (d, $^4J_{PH}$ = 1.2 Hz, 2 H, *m*-phenyl H); ^{13}C{^{1}H} NMR δ 9.56 (d, $^3J_{PC}$ = 5.5 Hz, $C_5(CH_3)_5$), 23.44 (dd, $^1J_{PC}$ = 48.3, 57.0 Hz, CH_2), 31.44 (s, *p*-$C(CH_3)_3$), 34.38 (d, J_{PC} = 2.7 Hz), 34.55 (d, J_{PC} = 3.3 Hz, *o*-$C(CH_3)_3$), 34.41 (s, *p*-$C(CH_3)_3$), 39.65 (s, *o*-$C(CH_3)_3$), 99.87 (s, $C_5(CH_3)_3$), 122.64 (s), 147.31 (s), 156.45 (s, aryl C), 202.46 (d, $^2J_{PC}$ = 7.9 Hz, RuCO), 203.09 (d, $^2J_{PC}$ = 6.2 Hz, RuCO); ^{31}P{^{1}H} NMR δ −110.57 (d, $|^1J_{PP}|$ = 167.2 Hz, PRu), −171.41 ($|^1J_{PP}|$ = 167.2 Hz, P aryl). Anal. Calcd for $C_{31}H_{46}O_2Ru$ (613.7): C, 60.67; H, 7.56. Found: C, 60.78; H, 8.03; Mol wt, 615 (MS/CI).

Path b. To a solution of 1.06 g (1.77 mmol) of **3b** was added 10 mL of THF an etheral 1 M CH_2N_2 solution dropwise. After 1 h of stirring at 20 °C it was worked up analogously to afford 0.101 g (9%) of **4b**.

(η^5-C_5Me_5)(CO)$_2$FePC(CH$_2$CH$_2$)PAr (5a). To a mixture of 1.93 g (3.50 mmol) of **3a** and 1.12 g (3.50 mmol) of [c-$C_3H_5SPh_2$]BF_4 in 30 mL of THF was added 0.43 g (3.50 mmol) of solid KO-*t*-Bu at 20 °C. The red-brown mixture was stirred for 18 h and then filtered, and the filtrate was freed from volatiles in vacuo. The residue was dissolved in 20 mL of petroleum ether and concentrated until the red solution became cloudy. At −28 °C 0.771 g of **5a** (37%) crystallized as yellow needles: IR (Nujol) 1982 (vs), 1939 (vs) (ν(CO)), 1586 (w), 1362 (m), 1279 (w), 1264 (m), 1240 (w), 1216 (w), 1199 (w), 1080 (m), 1028 (m), 913 (w), 903 (w), 892 (w), 870 (m), 807 (m), 795 (m), 750 (m), 740 (m), 692 (m), 638 (m), 590 (m) cm^{-1}; IR (cyclopentane) 1984 (vs), 1940 (vs) cm^{-1} (ν(CO)); ^{1}H NMR δ 0.74–2.04 (m, 4 H, $(CH_2)_2$), 1.30 (s, 9 H *p*-*t*-Bu), 1.42 (s, 15 H, $C_5(CH_3)_5$), 1.78 (s, 18 H, *o*-*t*-Bu), 7.47 (d, $^4J_{PH}$ = 1.9 Hz, *m*-phenyl H); ^{13}C{^{1}H} NMR δ 9.38 (d, $^3J_{PC}$ = 6.7 Hz, $C_5(CH_3)_5$), 14.08 (d, J_{PC} = 15.7 Hz), 14.92 (d (br), J_{PC} = 8.1 Hz, $(CH_2)_2$), 29.56 (dd, $^1J_{PC}$ = 67.4, 71.3 Hz, PCP), 31.50 (s, *p*-$C(CH_3)_3$), 34.12 (d, J_{PC} = 4.5 Hz), 34.27 (d, J_{PC} = 4.6 Hz, *o*-$C(CH_3)_3$), 34.56 (s, *p*-$C(CH_3)_3$), 39.28 (s, *o*-$C(CH_3)_3$), 95.69 (s, $C_5(CH_3)_5$), 121.59 (s), 142.96 (s), 156.54 (dd, J_{PC} = 1 Hz, aryl C), 216.88 (m, FeCO); ^{31}P{^{1}H} NMR δ −37.95 (d, $|^1J_{PP}|$ = 117.3 Hz, FeP), −133.38 (d, $|^1J_{PP}|$ = 117.3 Hz, P aryl); MS/CI (70 eV, 70 °C), *m/e* 594 (M$^+$), 566 (M$^+$ − CO), 538 (M$^+$ − 2CO), 482 (M$^+$ − 2CO − $Me_2C{=}CH_2$), 481 (M$^+$ − 2CO − *t*-Bu). Anal. Calcd for $C_{33}H_{48}FeO_2P_2$ (594.5): C, 66.67; H, 8.14; Fe, 9.39. Found: C, 66.39; H, 8.76; Fe, 9.22.

(η^5-C_5Me_5)(CO)$_2$RuPC(CH$_2$CH$_2$)PAr (5b). To the mixture of 1.40 g of **3b** and 0.73 g (2.33 mmol) of [c-$C_3H_5SPh_2$]BF_4 in 10 mL of THF was added a solution of 0.29 g (2.33 mmol) of KO-*t*-Bu in 10 mL of THF. The red-brown color of the solution darkened noticeably. It was filtered and worked up as described for **5a** to give 0.310 g (21%) of yellow **5b**: IR (Nujol) 1997 (vs), 1949 (vs) cm^{-1}, (ν(CO)), 1587 (m), 1238 (m), 1027 (m), 918 (w), 911 (w), 894 (w), 877 (w), 789 (s), 703 (s) cm^{-1}; IR (cyclopentane) 2018 (vs), 1963 (vs) cm^{-1} (ν(CO)); ^{1}H NMR δ 0.91–2.04 (m, 4 H, $(CH_2)_2$), 1.30 (s, 9 H, *p*-*t*-Bu), 1.58 (s, 15 H, $C_5(CH_3)_5$), 1.80 (s, 18 H, *o*-*t*-Bu), 7.37 (d, $^4J_{PH}$ = 1.9 Hz, 2 H, *m*-phenyl H); ^{13}C{^{1}H} NMR δ 9.66 (d, $^3J_{PC}$ = 5.1 Hz, $C_5(CH_3)_5$), 15.18 (d, $^2J_{PC}$ = 15.2 Hz, $(CH_2)_2$), 15.27 (dd, ^{2},J_{PC} = 4.1, 8.9 Hz, $(CH_2)_2$), 29.79 ("t", $^1J_{PC}$ = 70.0 Hz, PCP), 31.51 (s, *p*-$C(CH_3)_3$), 34.15 (d, $^4J_{PC}$ = 5.3 Hz, *o*-$C(CH_3)_3$), 34.31 (d, $^4J_{PC}$ = 4.1 Hz, *o*-$C(CH_3)_3$), 34.60 (s, *p*-$C(CH_3)_3$), 39.35 (s, *o*-$C(CH_3)_3$), 99.74 (s, $C_5(CH_3)_5$), 121.64 (s), 131.33 (s), 146.97 (s), 156.54 (s) (aryl C), 202.76 (s), 202.85 (s), 202.81 (d, $^2J_{PC}$ = 4.4 Hz, RuCO); ^{31}P{^{1}H} NMR δ −59.10 (d, $|^1J_{PP}|$ = 114.4 Hz, PRu), −128.64 (d, $^1J_{PP}$ = 114.4 Hz, PAr); MS/EI (70 eV, 70 °C), *m/e* 641 (M$^+$, relative to ^{102}Ru), 613 (M$^+$ − CO), 585 (M$^+$ − 2CO), 528 (M$^+$ − 2CO − *t*-Bu). Anal. Calcd for $C_{33}H_{48}O_2P_2Ru$ (639.8): C, 61.95; H, 7.56. Found: C, 61.87; H, 7.08.

X-ray Structure Determination of [(*E*)-(η^5-C_5Me_5)(CO)$_2$FePC(CH$_2$CH$_2$)PAr] (5a)

Crystals of **5a** were grown from *n*-pentane at −28 °C. An irregularly shaped crystal of the approximate dimensions 0.23 × 0.19 × 0.16 mm was sealed in a glass capillary and mounted at room temperature on a Nicolet R3 four-circle diffractometer (Mo Kα radiation, graphite monochromator). The cell dimensions were determined by refinement of the setting angles of 25 reflections (20° ≥ 2θ ≥ 25°): a = 8.344 (3) Å, b = 10.772 (4) Å, c = 19.005 (8) Å, α = 92.79 (3)°, β = 91.04 (3)°, γ = 93.69 (3)°, V = 1702.2 (1.0) Å^3. The space group was established to be $P\bar{1}$ (No. 2) by refinement (Z = 2, D_{calcd} = 1.1626 g/cm^3, μ = 5.60 cm^{-1}); ω-scan data collection of 7365 independent intensities ($2\theta_{max}$ = 45°), 5345 of which were treated as observed [$F_o \le 3.5\sigma(F)$]. The structure was solved by direct methods, successive difference Fourier maps, and least-squares cycles. Crystallographic programs were SHELXTL[15] with use of a NOVA 3/12 computer; scattering factors were taken from Cromer and Mann.[16] All non-hydrogen atoms were given anisotropic displacement parameters; the benzene ring and the methyl and methylene groups were treated as rigid groups (C–C = 1.395 Å, C–C–C = 120° and C–H = 0.96 Å, C–C–H =

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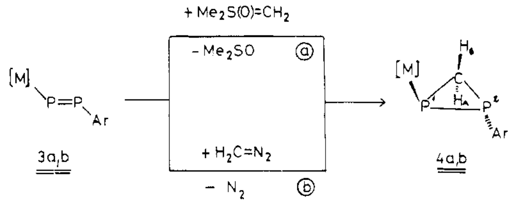
109.5°, respectively); the hydrogen atoms were given the 1.2-fold isotropic U value of the corresponding equivalent U_{ij} value of the bonded carbon atom. The R values, based on the final model refined with 386 parameters, were $R = \sum(||F_o| - |F_c||/\sum|F_o|) = 0.077$ and $R_w = (\sum||F_o| - |F_c||^2/\sum w|F_o|^2)^{1/2} = 0.086$, where $w^{-1} = (\sigma^2(F_o) + 1.36 \times 10^{-3}F_o^2)$. The maximum residual electron density was 1.25 e/Å^3 at a distance of 0.39 Å from C6.

Results and Discussion

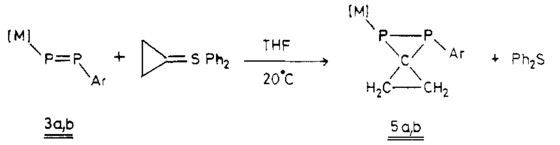
Activated carbon–carbon double bonds are effectively cyclopropanated by sulfur ylides. We have extended this synthetic approach to the phosphorus–phosphorus double bond in transition-metal-activated diphosphenes. The iron and ruthenium compounds **3a** and **3b**, respectively, smoothly react with an excess of the sulfur ylide $Me_2S(O){=}CH_2$ in THF at ambient temperature to give the orange-yellow microcrystalline diphosphiranes **4a** and **4b** in 45% and 32% yield, respectively. The same compounds **4** are also accessible by treatment of **3a,b** with an excess of CH_2N_2 albeit in smaller yields. The course of the reaction is conveniently monitored by ^{31}P NMR spectroscopy. The two low-field doublets of the starting material are replaced by two doublets in the characteristic high-field region for strained three-membered rings. Possible intermediates of the reaction could not be detected. The compounds **4a,b** are isolated by means of column chromatography and are stable at 20 °C under an N_2 atmosphere.



(4)

Ar = 2,4,6-tri-*tert*-butylphenyl; **a**, [M] = $Fe(CO)_2(\eta^5\text{-}C_5Me_5)$; **b**, [M] = $Ru(CO)_2(\eta^5\text{-}C_5Me_5)$

The first 1,2-diphosphaspiro[2.2]pentanes were obtained by the reaction of **3a,b** with equimolar amounts of diphenylsulfonium cyclopropanide generated from the corresponding sulfonium salt and potassium *tert*-butoxide in THF at room temperature. It is noteworthy that the transformation of the ruthenium derivative is considerably faster than that of the iron complex. Orange-yellow, thermally stable **5a,b** are isolated by fractional crystallization. The complex $(\eta^5\text{-}C_5H_5)(CO)(PPh_3)FeP{=}PAr$[11] cannot be cyclopropanated under these conditions, which is presumably due to the easy dissociation of the triphenylphosphine ligand.



(5)

The products **4**, **5a**, and **5b** were initially characterized by elemental analyses and spectroscopic methods (IR, ^1H, ^{13}C, and ^{31}P NMR, MS). Mass spectra (EI) revealed the monomeric character of the compounds. The presence of unsymmetrically substituted diphosphiranes is confirmed by the ^{31}P NMR spectra of **4a**, **4b**, **5a**, and **5b**. Two doublets at high field (**4a**, $\delta(P_1)$ −91.97, $\delta(P_2)$ −177.47 ($^1J_{P_1P_2}$ = 170.9 Hz); **4b**, $\delta(P_1)$ −110.57, $\delta(P_2)$ −171.41 ($^1J_{P_1P_2}$ = 167.2 Hz), **5a**; $\delta(P_1)$ −37.95, $\delta(P_2)$ −133.38 ($^1J_{P_1P_2}$ = 117.3 Hz); **5b**, $\delta(P_1)$ −59.10, $\delta(P_2)$ −128.64 ($^1J_{P1P2}$ = 114.4 Hz) are diagnostic for three-membered strained phosphorus ring compounds.[3b]

Table I. Atomic Coordinates (×10^4) and Equivalent Isotropic Thermal Parameters (Å^2 × 10^3)^a for 5a

atom	x	x	z	U
Fe	2720 (1)	8094 (1)	8816 (1)	50 (1)
P(1)	2445 (1)	6451 (1)	7984 (1)	49 (1)
P(2)	4846 (1)	5868 (1)	7695 (1)	46 (1)
C(1)	4284 (6)	7406 (5)	9241 (3)	66 (2)
O(1)	5314 (5)	7005 (4)	9541 (2)	99 (2)
C(2)	4006 (7)	8927 (5)	8255 (3)	74 (2)
O(2)	4822 (6)	9517 (4)	7917 (3)	114 (2)
C(3)	3400 (6)	5105 (4)	8272 (2)	55 (1)
C(4)	2667 (8)	3786 (4)	8288 (3)	75 (2)
C(5)	3439 (9)	4413 (6)	8932 (3)	86 (2)
C(6)	4581^b	4823^b	6846^b	46 (1)
C(7)	3331 (3)	4994 (2)	6372 (2)	47 (1)
C(8)	2619^b	3975^b	5974^b	54 (1)
C(9)	3157^b	2786^b	6051^b	51 (1)
C(10)	4408^b	2616^b	6525^b	52 (1)
C(11)	5120^b	3634^b	6923^b	48 (1)
C(12)	3012 (6)	6299 (4)	6065 (2)	55 (2)
C(13)	3347 (8)	6226 (5)	5265 (3)	80 (2)
C(14)	1237 (7)	6549 (5)	6165 (3)	81 (2)
C(15)	4094 (7)	7394 (4)	6370 (3)	73 (2)
C(16)	2220 (6)	1613 (4)	5719 (3)	61 (2)
C(17)	3334 (10)	851 (7)	5305 (4)	129 (4)
C(18)	748 (11)	1881 (6)	5340 (5)	150 (4)
C(19)	1584 (9)	743 (6)	6303 (4)	110 (3)
C(20)	6832 (6)	3438 (4)	7252 (3)	60 (2)
C(21)	7450 (8)	2162 (6)	7000 (4)	99 (3)
C(22)	8041 (6)	4479 (6)	7008 (3)	84 (2)
C(23)	6853 (7)	3453 (6)	8050 (3)	87 (2)
C(24)	1831 (7)	9021 (6)	9705 (3)	86 (2)
C(25)	1073 (7)	7855 (5)	9629 (3)	72 (2)
C(26)	253 (7)	7695 (6)	9038 (3)	78 (2)
C(27)	425 (9)	8709 (8)	8660 (3)	121 (4)
C(28)	1460 (10)	9633 (5)	9093 (6)	141 (4)
C(29)	2776 (10)	9525 (14)	10348 (6)	265 (7)
C(30)	1046 (13)	6818 (9)	10161 (5)	187 (6)
C(31)	−855 (9)	6558 (10)	8811 (6)	203 (6)
C(32)	−360 (17)	8952 (18)	7973 (5)	386 (11)
C(33)	1966 (21)	10965 (7)	8975 (11)	433 (12)

^{a} U defined as one-third of the trace of the orthogonalized U_{ij} tensor. ^{b} In rigid groups without standard deviations.

It is evident that the phosphorus nuclei in the spiro compounds **5a,b** experience significantly less shielding than in **4a,b**. A similar effect was observed by Baudler in going from **1a** (δ −168.8 ppm)[3a,c,17] to $(t\text{-BuP})_2C(t\text{-BuP})_2$ (δ −132.0).[6] This is an indication for an increasing widening of the exocyclic bond angles at phosphorus with increasing steric encumbarance by the ring substituents, which generally causes the deshielding of the ^{31}P nuclei. A doublet of doublets at δ 23.03 ($^1J_{PC}$ = 48.6, 60.2 Hz) in the ^{13}C NMR spectrum of **4a** is in accordance with the proposed three-membered-ring structure. In $Ar\overline{P\text{-}CH_2\text{-}P}Ar$ this carbon atom is observed as a triplet at $\delta(^{13}C)$ 32.54 ($^1J_{PC}$ = 24 Hz) whereas in **1a** values of $\delta(^{13}C)$ 6.2 and $^1J_{PC}$ = 53.0 Hz are encountered. The quaternary carbon atom in **5a** gives rise to a doublet of doublets at $\delta(^{13}C)$ 29.56 ($^1J_{PC}$ = 67.4, 71.3 Hz). In $(t\text{-BuP})_2C(t\text{-BuP})_2$ this carbon atom resonates as a quintet at $\delta(^{13}C)$ 24.46 (^1J_P = 80.6 Hz).[6] Again the higher ring substitution leads to a noticeable deshielding ($\Delta\delta(^{13}C)$ = 6.53 ppm as compared to that in **4a**). Two doublets at $\delta(^{13}C)$ 14.08 ($^2J_{PC}$ = 15.7 Hz) and $\delta(^{13}C)$ 14.92 ($^2J_{PC}$ = 8.1 Hz) in **5a** are assigned to the carbon atoms of the $C(CH_2)_2$ moiety. The CH_2 protons of **4b** appear as two doublets of doublets at $\delta(^1H_A)$ 1.78 and $\delta(^1H_B)$ 2.26 in the ^1H NMR spectrum. Besides the geminal coupling ($^2J_{AB}$ = 8.8 Hz) each proton is additionally coupled to the phosphorus atom with the trans-oriented ligand

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Table II. Selected Bond Lengths (Å) of 5a

Fe–P(1)	2.310 (1)	P(1)–C(3)	1.799 (5)
Fe–C(1)	1.748 (5)	P(2)–C(3)	1.824 (5)
Fe–C(2)	1.760 (6)	P(2)–C(6)	1.921 (3)
Fe–C(24)	2.084 (6)	C(1)–O(1)	1.142 (7)
Fe–C(25)	2.097 (6)	C(2)–O(2)	1.129 (7)
Fe–C(26)	2.130 (5)	C(3)–C(4)	1.510 (6)
Fe–C(27)	2.087 (8)	C(3)–C(5)	1.489 (7)
Fe–C(28)	2.067 (7)	C(4)–C(5)	1.485 (8)
P(1)–P(2)	2.206 (2)		

Table III. Selected Bond Angles (deg) of 5a

P(1)–Fe–C(1)	91.2 (2)	Fe–C(1)–O(1)	176.7 (5)
P(1)–Fe–C(2)	90.2 (2)	Fe–C(2)–O(2)	176.3 (5)
C(1)–Fe–C(2)	94.0 (3)	P(1)–C(3)–P(2)	75.0 (2)
Cp[a]–Fe–P(1)	118.3	P(1)–C(3)–C(4)	127.1 (4)
Cp[a]–Fe–C(1)	124.7	P(2)–C(3)–C(4)	133.1 (4)
Cp[a]–Fe–C(2)	128.3	P(1)–C(3)–C(5)	135.8 (4)
Fe–P(1)–P(2)	109.3 (1)	P(2)–C(3)–C(5)	137.4 (4)
Fe–P(1)–C(3)	111.7 (1)	C(4)–C(3)–C(5)	59.4 (4)
P(2)–P(1)–C(3)	53.0 (2)	C(3)–C(4)–C(5)	59.6 (3)
P(1)–P(2)–C(3)	52.0 (2)	C(3)–C(5)–C(4)	61.0 (3)
P(1)–P(2)–C(6)	107.1 (1)	P(2)–C(6)–C(7)	120.0 (1)
C(3)–P(2)–C(6)	101.6 (2)	P(2)–C(6)–C(11)	112.8 (1)

[a] Centroid of cyclopentadienyl ring.

and the cis-configurated phosphorus lone pair. The resonances of the $C(CH_2)_2$ protons are partly obscured by the *tert*-butyl and $(CH_3)_5C_5$ signals and cannot be located unambigiously. Complexes **4a**, **4b**, **5a**, and **5b** display two intense ν(CO) bands for the $M(CO)_2$ groups at 1996 and 1949 cm^{-1} (**4a**), 2016 and 1959 cm^{-1} (**4b**), 1984 and 1940 cm^{-1} (**5a**), and 2018 and 1963 cm^{-1} (**5b**).

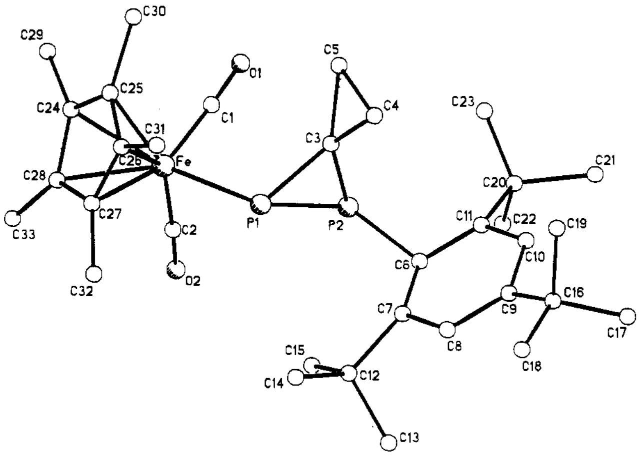

Figure 1. Molecular structure of $(\eta^5\text{-}C_5Me_5)(CO)_2FePC(CH_2CH_2)PAr$ (**5a**).

X-ray Structure Analysis of 5a

The X-ray structure analysis of **5a** fully confirms the conclusions derived from analyses and spectroscopic data. The results of the structural determinations are shown in Figure 1. Positional parameters for the complex are given in Table I, and derived distances and angles are presented in Tables II and III, respectively.

The analysis confirms the presence of the 1,2-diphosphaspiro[2.2]pentane system linked to the metal through a Fe–P single bond [2.310 (1) Å]. This distance is significantly longer than the Fe–P bond length in **3a** [2.260

Table IV. Anisotropic Thermal Parameters (Å² × 10³) for 5a[a]

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe	55 (1)	43 (1)	50 (1)	–3 (1)	11 (1)	–5 (1)
P(1)	55 (1)	41 (1)	50 (1)	–1 (1)	4 (1)	–2 (1)
P(2)	53 (1)	41 (1)	43 (1)	–0 (1)	0 (1)	–3 (1)
C(1)	67 (3)	74 (3)	54 (3)	–14 (2)	2 (2)	2 (3)
O(1)	84 (3)	122 (4)	91 (3)	–15 (3)	–27 (2)	22 (3)
C(2)	90 (4)	55 (3)	76 (3)	–9 (2)	29 (3)	–11 (3)
O(2)	136 (4)	88 (3)	113 (4)	–1 (3)	60 (3)	–44 (3)
C(3)	69 (3)	43 (2)	51 (2)	6 (2)	6 (2)	–5 (2)
C(4)	98 (4)	42 (2)	85 (4)	12 (3)	24 (3)	–5 (3)
C(5)	119 (5)	74 (4)	70 (4)	28 (3)	24 (3)	18 (3)
C(6)	46 (2)	37 (2)	53 (2)	4 (2)	–4 (2)	2 (2)
C(7)	58 (3)	34 (2)	50 (2)	3 (2)	–5 (2)	8 (2)
C(8)	64 (3)	47 (2)	51 (2)	–2 (2)	–12 (2)	9 (2)
C(9)	58 (3)	39 (2)	56 (3)	–6 (2)	–8 (2)	5 (2)
C(10)	58 (3)	42 (2)	57 (3)	–1 (2)	–6 (2)	14 (2)
C(11)	49 (2)	43 (2)	52 (2)	3 (2)	–4 (2)	4 (2)
C(12)	75 (3)	45 (2)	49 (2)	11 (2)	–1 (2)	15 (2)
C(13)	131 (5)	62 (3)	49 (3)	16 (2)	1 (3)	19 (3)
C(14)	103 (5)	64 (3)	81 (4)	12 (3)	–6 (3)	36 (3)
C(15)	112 (4)	39 (2)	68 (3)	14 (2)	3 (3)	5 (3)
C(16)	67 (3)	46 (2)	68 (3)	–8 (2)	–5 (2)	–2 (2)
C(17)	118 (6)	97 (5)	163 (8)	–71 (5)	14 (5)	–13 (4)
C(18)	154 (8)	69 (4)	222 (10)	–25 (5)	–127 (7)	8 (4)
C(19)	119 (6)	70 (4)	138 (6)	3 (4)	2 (5)	–19 (4)
C(20)	55 (3)	62 (3)	65 (3)	0 (2)	–10 (2)	17 (2)
C(21)	73 (4)	102 (5)	124 (6)	–15 (4)	–23 (4)	45 (4)
C(22)	45 (3)	107 (5)	99 (4)	3 (4)	–7 (3)	–2 (3)
C(23)	78 (4)	109 (5)	76 (4)	20 (3)	–17 (3)	27 (3)
C(24)	68 (4)	95 (4)	89 (4)	–50 (4)	27 (3)	–12 (3)
C(25)	73 (4)	75 (3)	68 (3)	4 (3)	21 (3)	1 (3)
C(26)	56 (3)	90 (4)	87 (4)	–19 (3)	9 (3)	2 (3)
C(27)	126 (6)	196 (8)	56 (3)	15 (4)	12 (4)	114 (6)
C(28)	162 (7)	40 (3)	231 (9)	36 (4)	148 (7)	34 (4)
C(29)	79 (5)	452 (19)	231 (11)	–268 (12)	20 (6)	–25 (8)
C(30)	241 (11)	162 (8)	181 (9)	95 (7)	153 (8)	82 (8)
C(31)	81 (5)	248 (12)	253 (12)	–167 (10)	60 (6)	–70 (6)
C(32)	358 (16)	783 (29)	82 (6)	108 (12)	56 (8)	459 (19)
C(33)	531 (21)	56 (5)	750 (27)	124 (10)	553 (21)	105 (9)

[a] The temperature factor exponent has the form -2^{-2} $(h^2a2U_{11} + \cdots + 2hkabU_{12})$.

Table V. Hydrogen Atom Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3)^a

	x	*y*	*z*	*U*
H(4a)	3321	3160	8029	92
H(4b)	1530	3617	8224	92
H(5a)	4419	4144	9126	99
H(5b)	2754	4665	9307	99
H(8)	1452 (56)	4204 (45)	5517 (25)	78 (11)
H(10)	5003 (58)	1801 (46)	6530 (26)	78 (11)
H(13a)	2573	5680	5003	97
H(13b)	4406	5961	5177	97
H(13c)	3276	7063	5119	97
H(14a)	868	6588	6642	93
H(14b)	569	5943	5889	93
H(14c)	1183	7352	5970	93
H(15a)	3927	7645	6854	90
H(15b)	3845	8058	6074	90
H(15c)	5194	7207	6309	90
H(17a)	3201	1419	4937	154
H(17b)	2817	52	5166	154
H(17c)	4457	763	5389	154
H(18a)	1228	2205	4925	168
H(18b)	32	2466	5536	168
H(18c)	158	1103	5219	168
H(19a)	2540	465	6516	134
H(19b)	963	39	6088	134
H(19c)	960	1143	6658	134
H(21a)	7520	1976	6502	124
H(21b)	6808	1511	7210	124
H(21c)	8508	2220	7210	124
H(22a)	8008	4353	6504	103
H(22b)	9103	4358	7182	103
H(22c)	7766	5312	7136	103
H(23a)	6582	4246	8253	106
H(23b)	7875	3250	8236	106
H(23c)	6057	2822	8164	106
H(29a)	3170	10379	10430	219
H(29b)	3625	8987	10435	219
H(29c)	1906	9341	10659	219
H(30a)	1663	7490	10410	216
H(30b)	1639	6081	10152	216
H(30c)	49	6659	10396	216
H(31a)	−1628	6795	8471	226
H(31b)	−1403	6217	9206	226
H(31c)	−206	5942	8598	226
H(32a)	76	9727	7804	369
H(32b)	−1482	9009	8062	369
H(32c)	−223	8292	7624	369
H(33a)	1458	11034	8523	432
H(33b)	3101	11150	8939	432
H(33c)	1534	11545	9311	432

^{a} Atoms in rigid groups without standard deviations.

(1) Å].[11] Usually Fe–P bond distances in low-valent carbonyliron complexes fall in the range of 2.17–2.35 Å.[18]

The ligand could be regarded as one leg in a slightly distored three-legged piano-stool arrangement. The three angles the ligands form with the metal center are P(1)–Fe–C(1) = 91.2 (2)°, C(1)–Fe–C(2) = 94.0 (3)°, and P(1)–Fe–C(2) = 90.2 (2)°.

Two legs of the piano stool are represented by terminal, nearly linear, carbonyl groups. The most interesting structural feature of **5a** is the geometry of the novel 1,2-diphosphaspiro[2.2]pentanide ligand, which is attached to the iron via the phosphorus atom P(1). This ligand consists of a cyclopropane and a diphosphirane ring. The planes of both three-membered rings are nearly orthogonal (ψ = 93.1°). The cyclopropane ring is close to an equilateral triangle ($\bar{d}$(C–C) = 1.498 (4) Å; C–C–C = 60 ± 1°) with no significant differences in the cyclic bond distances; however they are comparable with those in spiropentane itself[19] (distances from the spiro atom to methylene atoms, 1.477 Å, and between methylene atoms, 1.527 Å, and angles at the spiro atom, 62.2°). In the $P_2C(3)$ triangle the P–P distance (2.206 (2) Å) is expectedly larger than the P–C distances (P(1)–C(3) = 1.799 (5) Å; P(2)–C(3) = 1.824 (5) Å). This causes a widening of the angle P(1)–C(3)–P(2) to 75.0 (2)°, whereas the endocyclic angles at the phosphorus atom are compressed to 52.0 (2)° and 53.0 (2)°, respectively. A similar situation was encountered in the tetraphosphaspiro[2.2]pentane $(t\text{-BuP})_2C(t\text{-BuP})_2$.[20] There, however, the P–P single bond is considerably shortened (2.175 ppm) as compared to that in **5a**. The P–P distance of **5a** more closely resembles the one in $(t\text{-BuP})_2C{=}C(4\text{-ClC}_6H_4)_2$ (2.198 Å).[4] A value of 2.225 Å represents an average phosphorus–phosphorus single-bond distance of numerous structures.[21] The endocyclic P–C bonds (average 1.812 (5) Å) are markedly shorter than the exocyclic distance P(2)–C(6) (1.921 (3) Å). The exocyclic angles at P(1) (Fe–P(1)–C(3) = 111.7 (1)°; Fe–P(1)–P(2) = 109.3 (1)° indicate a slightly ψ-tetrahedral distortion which is less pronounced at P(2) (C(3)–P(2)–C(6) = 101.6 (2)°; P(1)–P(2)–C(6) = 107.1 (1)°). In the starting material **3a** the atoms Fe, P(1), P(2), and C(6) are arranged in the same plane. This is no longer true for 5a where C(6) deviates out of the plane of the remaining atoms by 0.463 Å (torsion angle Fe–P(1)–P(2)–C(6) = −165.4°).

Conclusions

This paper not only presents a novel synthetic approach to diphosphiranes and a first synthesis and structure determination of a 1,2-diphosphaspiro[2.2]pentane derivative but also underlines once more the close chemical relation of P=P and C=C double bonds as invoked by the concepts of diagonal relationship and isoelectronic molecules. Furthermore the scope of application of sulfur ylides is extended from the organic[10] and organometallic chemistry[12] to the inorganic chemistry of other main-group elements.[23]

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Acknowledgment. This work has been supported by the Deutsche Forschungsgemeinschaft, Bonn, Fonds der Chemischen Industrie, Frankfurt; and the DEGUSSA AG, Hanau, Germany, which are gratefully acknowledged.

Registry No. **3a**, 98088-31-4; **3b**, 98088-32-5; **4a**, 112713-06-1; **4b**, 112713-07-2; **5a**, 112713-09-4; **5b**, 112713-08-3; $Me_2S(O{=}CH_2$, 70775-39-2; $[C\text{-}C_3H_5SPh_2)BF_4$, 33462-81-6.

Supplementary Material Available: Tables of crystal data, atom coordinates and isotropic thermal parameters, bond distances, bond angles, anisotropic thermal parameters, and hydrogen atom coordinates and isotropic thermal parameters (9 pages); a listing of observed and calculated structure factors (44 pages). Ordering information is given on any current masthead page.

Cationic Complexes of Rhodium(I) and Iridium(I) with Methyl- and Phenylbis(dimethoxyphosphino)amine

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Received September 21, 1987

The ligand $PhN(P(OMe)_2)_2$ (L_2) reacts with $[Rh(COD)(acetone)_x]ClO_4$ to form $[Rh(COD)(L_2)]ClO_4$, $[Rh(L_2)_2]ClO_4$, and $[Rh_2(L_2)_4(\mu\text{-}L_2)](ClO_4)_2$ depending on the metal/ligand ratio used. By contrast $MeN(P(OMe)_2)_2$ (L_2') only forms $[Rh_2(L_2')_2(\mu\text{-}L_2')_2]^{2+}$ which was isolated as PF_6^-, BPh_4^-, ClO_4^-, and $F_3CSO_3^-$ salts. Other rhodium complexes of the latter ligand that were synthesized include $[Rh(L_2')(DPPE)]ClO_4$, $[Rh(L)(L_2')(DPPE)]ClO_4$ (L = CO, $P(OMe)_3$), and $[Rh_2(L_2')_2(\mu\text{-}L_2'')_2](ClO_4)_2$ (L_2'' = 2,5-bis(diphenylphosphino)furan). The iridium analogue of the latter was also prepared as were several iridium complexes of $MeN(P(OMe)_2)_2$ including $[Ir(L_2')(PPh_3)_2]ClO_4$, $[Ir(L_2')_2(PPh_3)]ClO_4$, $[Ir(CO)(L_2')(PPh_3)_2]ClO_4$, $[Ir(L_2')_3]ClO_4$, and $[Ir(L_2')(BDPPF)]ClO_4$. The last appears to form five-coordinate adducts with O_2 and dimethyl acetylenedicarboxylate. With the exception of these last two, all the five-coordinate complexes prepared are proposed to adopt fluxional trigonal-bipyramidal structures. $[Ir(CO)(L_2')(PPh_3)_2]ClO_4$ crystallizes in the monoclinic system with space group $P2_1/c$, a = 16.067 (2) Å^2, b = 14.421 (2) Å, c = 1.9574 (4) Å, β = 102.49 (1)°, and Z = 4. Full-matrix least-squares refinement of 341 variables using 5462 data ($I > 3\sigma(I)$) led to final values of R and R_w of 0.037 and 0.048, respectively. The perchlorate ion is partially disordered. The complex adopts a distorted trigonal-bipyramidal structure with an equatorial carbonyl ligand. $[Rh_2(L_2')_4](F_3CSO_3)_2$ crystallizes in the monoclinic system with space group $P2_1/c$, a = 22.676 (4) Å, b = 19.079 (4) Å, c = 12.236 (7) Å, β = 97.12 (3)°, and Z = 4. Full-matrix least-squares refinement of 523 variables using 6097 data ($I > 3\sigma(I)$) led to final values of R and R_w of 0.055 and 0.083, respectively. One anion is severely disordered. The dimer cation contains two distorted square-planar rhodium atoms bridged by two $MeN(P(OMe)_2)_2$ ligands situated cis to one another. The coordination sphere of each metal is completed by a second ligand which chelates resulting in a basket-shaped species.

Introduction

We have been engaged for several years in studies on the synthesis of binuclear complexes of the short-bite ligands bis(diphenylphosphino)methane (DPM) and its arsenic analogue (DAM) and their reactivity toward small organic and inorganic molecules.[1] From this work and related studies by others[2] it has become increasingly evident that the bulk of the phenyl groups on these ligands significantly restricts access to the metal atoms. In considering sterically less-demanding ligands with which it was hoped to prepare related binuclear complexes that would have the potential to bind a larger variety of substrates we chose $MeN(P(OMe)_2)_2$.[3] This was attractive because of its relative ease of synthesis and handling and because it had already been found to form a binuclear complex of cobalt[3] while $EtN(P(OMe)_2)_2$ also formed suitable binuclear rhodium complexes.[4] Apart from this brief report and others on rhodium complexes of $EtN(P(OPh)_2)_2$[5] and iridium complexes of $RN(PPh_2)_2$ (R = H, Me, Ph, β-tolyl)[6] the ligating properties of this class of ligands toward platinum group metals has not been investigated. We report here on the results of our efforts to expand this area which, unfortunately, did not yield any of the desired binuclear complexes.

Experimental Section

All solvents were appropriately dried and distilled prior to use and were stored under dinitrogen. All operations were performed under a dinitrogen atmosphere although most of the products proved not be to particularly sensitive to the ambient atmosphere. Standard Schlenk techniques were used. Hydrated rhodium(III) chloride, silver perchlorate, and silver trifluoromethanesulfonate

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0276-7333/88/2307-0983$01.50/0