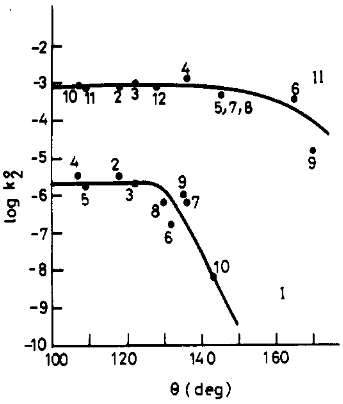


Figure 10. Steric profile for (η^5-C_5Me_5)Co(CO)$_2$ (I) and (η^5-$C_5H_4CO_2Me$)Co(CO)$_2$ (II) at 70.0 °C. The numbers correspond to those in the paper reported by Basolo and co-workers[4a] and to those in Table IV, respectively.

(136°); thus, as expected, the transition state is more congested in the former complex.

On the other hand, the smaller steric sensitivity (0.078) for the carbomethoxy complex indicates that its ability to sterically accommodate the incoming ligand is higher; that is, (η^5-$C_5H_4CO_2Me$)Co(CO)$_2$ is more flexible than (η^5-C_5Me_5)Co(CO)$_2$, which can be attributed to a greater degree of ring slippage $\eta^5 \rightarrow \eta^3$ in the former caused by the electron-withdrawing carbomethoxy substituent in the ring.

These results about the steric properties and intrinsic reactivity of both complexes are qualitatively similar to those obtained when the analysis of kinetics data is based on pK_a values. The intrinsic reactivity is log k_2 for a particular small nucleophile corrected to what it would be for a standard nucleophile with pK_a = 0.[22,23] Pöe[18] has proposed that it is useful to use a less basic hypothetical nucleophile as a reference standard, on the grounds that the rate for a less basic nucleophile is determined more by the complex itself than by the nucleophile.

He has chosen to use as a standard a hypothetical very weak nucleophile with pK_a = −4. This is less basic than any of the P-donors available[11] and will provide reasonable estimation of intrinsic reactivities.

The plot of log $k_2 - a(\mathrm{p}K_a + 4) = \log k_2^\circ$ against θ (Figure 10) allows us to obtain the value of $[\log k_2^\circ]_{\theta\to 0}$ (intrinsic reactivity) after the a value has been determined.

We use the value $a = 0.22$ obtained by Giering[10] for the (η^5-C_5Me_5)Co(CO)$_2$ complex and the value $a = 0.25$ for the (η^5-$C_5H_4CO_2Me$)Co(CO)$_2$ obtained from the electronic profile generated from the isosteric (θ = 145°) triarylphosphine data points. As is shown in Figure 10, the difference ($\Delta \simeq 2.5$) in the intrinsic reactivity of both complexes is similar to that obtained above.

The steric effects for (η^5-C_5Me_5)Co(CO)$_2$ become evident at a cone angle (θ_{st} = 120–125°) smaller than that for (η^5-$C_5H_4CO_2Me$)Co(CO)$_2$ (θ_{st} = 140–145°). Above this cone angle range, the sharp and gradual changes for the pentamethyl and carbomethoxy complexes respectively indicate that the latter is more flexible than the former.

Acknowledgment. We thank Dr. Jesús H. Rodriguez Ramos for the ^{1}H NMR spectra. We also thank Prof. W. P. Giering for helpful comments and express our great appreciation of financial support from the Dirección General de Investigación Científica y Técnica (Spain).

---

(22) Jackson, R. A.; Kanluen, R.; Pöe, A. J. *Inorg. Chem.* **1984**, *23*, 523.
(23) Dahlinger, K.; Falcone, F.; Pöe, A. J. *Inorg. Chem.* **1986**, *25*, 2654.

Transition-Metal-Substituted Diphosphenes. 21.[1] [2 + 2] Cycloaddition of a Diphosphene to Maleimide and *N*-Methylmaleimide. X-ray Structure Analysis of a 4,5-Diphospha-2-azabicyclo[3.2.0]hepta-1,3-dione

Lothar Weber,* Matthias Frebel, Achim Müller, and Hartmut Bögge

Fakultät für Chemie der Universität Bielefeld, D-4800 Bielefeld 1, Germany

Received July 23, 1990

The reaction of [(η^5-C_5Me_5)(CO)$_2$FeP=P—aryl (aryl = 2,4,6-t-$Bu_3C_6H_2$) with maleimide and N-methylmaleimide in benzene at 75 °C afforded the transition-metal-functionalized orange-red 1,2-diphosphetanes (η^5-C_5Me_5)(CO)$_2$Fe–P[C(H)C(O)N(R)C(O)CH]P-aryl, **3** (R = H) and **4** (R = CH_3), as a mixture of diastereoisomers. They result from an endo and/or exo [2 + 2] cycloaddition of the P=P double bond of **1** to the C=C functionality of the imides. The novel compounds were characterized by elemental analyses and spectroscopic methods (IR, ^{1}H, ^{13}C, and ^{31}P NMR, and mass spectroscopy). The molecular structure of the major isomer of 1,2-diphosphetane (η^5-C_5Me_5)(CO)$_2$Fe–P[C(H)C(O)N(CH_3)C(O)CH]P-aryl·0.5(C_2H_5)$_2$O (**4b**) was elucidated by a complete single-crystal diffraction study [$C2/c$ space group; Z = 8, a = 31.465 (7) Å, b = 14.131 (3) Å, c = 17.277 (3) Å, β = 94.850 (15)°].

Introduction

Low-coordinated phosphorus compounds as, e.g., diphosphenes $R^1P{=}PR^2$, are potential candidates for ambident reactivity, because they possess two high-lying molecular orbitals [π and n(P)] of similar energy.[2] The introduction of an electron-releasing metal fragment at the phosphorus center raises the energy of the n(P) orbital considerably and thus renders a nucleophilic low-coordinated P atom. In keeping with this, diphosphene **1** un-

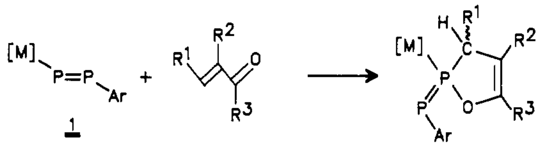
---

(1) Part 20: Weber, L.; Schumann, H. *Chem. Ber.* **1991**, *124*, 265.

(2) Review: (a) Cowley, A. H. *Polyhedron* **1984**, *3*, 389. (b) Cowley, A. H.; Norman, N. C. *Progr. Inorg. Chem.* **1986**, *34*, 1.

0276-7333/91/2310-1130$02.50/0

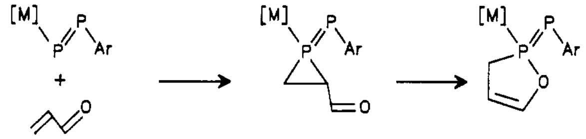
dergoes cheletropic [1 + 4] cycloadditions to the α,β-unsaturated carbonyls acrolein, methylacrolein, 3-buten-2-one, and crotonaldehyde to afford dihydro-1,2λ^5-oxaphospholes **2** with exocyclic P=P bonds.[3]



(1)

M = (η^5-C_5Me_5)$(CO)_2$Fe; (η^5-C_5Me_5)$(CO)_2$Ru; R^1, R^2, R^3 = H, Me

For the cheletropic [1 + 4] cycloaddition, it is crucial that the α,β-unsaturated carbonyl can adopt a cisoid conformation. In our case, it is not clear whether this reaction is a concerted process or whether it proceeds via a [1 + 2] cycloaddition that is rapidly followed by ring expansion.[4]



It was anticipated that α,β-unsaturated carbonyls with a rigid arrangement of the diene system might lead to stable phosphiranes.

Here we report on the reactions of diphosphene (η^5-C_5Me_5)$(CO)_2$Fe—P=P-aryl (aryl = 2,4,6-*t*-$Bu_3C_6H_2$) (**1**) with maleimide, and *N*-methylmaleimide.

Experimental Section

General Information. Standard inert-atmosphere techniques were used for the manipulation of all reagents and reactions products. Infrared spectra were recorded on a Perkin-Elmer Model 597 spectrometer. ^1H, ^{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 taken on a Varian MAT 312 spectrometer.

Materials. The diphosphenyl complex (η^5-C_5Me_5)$(CO)_2$FeP=PAr (Ar = 2,4,6-*t*-$Bu_3C_6H_2$)[5] was prepared as described in the literature, whereas maleimide and *N*-methylmaleimide were purchased commercially. All solvents were rigorously dried with an appropriate drying agent and distilled before use.

Reaction of 1 with Maleimide. Solid freshly sublimed maleimide (0.36 g, 3.75 mmol) was added to a solution of 0.83 g (1.50 mmol) of **1** in 45 mL of benzene at ambient temperature. The mixture was heated at 70–75 °C for 24 h, and after it was cooled to 20 °C, it was freed from all volatiles in vacuo. The dark brown oily residue was taken up in 50 mL of pentane and filtered. The filter cake was repeatedly extracted with pentane until the extracts were colorless. The combined dark red extracts were concentrated to 100 mL and subjected to fractional crystallization at -28 °C. The collected crops of red crystals were recrystallized from pentane to give 0.370 g (38%) of a diastereomeric mixture **3a** and **3b** (1:2), which could preparatively not be separated.

IR (cyclopentane): 1997 vs, 1952 vs [ν(Fe(CO)], 1760 m, br, 1739 m, 1725 s, 1705 s cm^{-1} [$\nu(CO)_{acyl}$]. IR (Nujol): 2033 w, 1995 vs, 1943 sh, 1941 vs [ν(Fe(CO)], 1760 w, 1720 w br, 1690 s, br [$\nu(CO)_{acyl}$], 1337 s, 1168 w, 871 w, 742 w, 633 w, 586s, 584 sh, 509 w cm^{-1}. ^1H NMR: δ 1.32 (s, 9 H, *p*-*t*-Bu of **3a**), 1.45 (s, 9 H, *p*-*t*-Bu of **3b**), 1.50 [s, 15 H, $C_5(CH_3)_5$ of **3a** and **3b**], 1.63 s, 1.66 s, 1.84 (s, *o*-*t*-Bu of **3a** and **3b**), 2.82–2.91 (m, 1 H, CH_{ring} of **3b**), 3.40–3.63 (m, CH_{ring} of **3b** and C_2H_{2ring} of **3a**), 7.45 (d, *J* = 2 Hz, 1 H, *m* aryl H of **3b**), 7.54 (s, br, 1 H, *m* aryl H of **3b**), 7.57 (s br, 1 H *m* aryl H of **3a**), 7.59 (s br, 1 H, *m* aryl H of **3a**), 8.70 (s, 1 H, NH of **3b**), 9.19 (s, 1 H, NH). $^{13}C\{^1H\}$ NMR: δ 9.15 [s, $C_5(CH_3)_5$ of **3a**], 9.33 [s, $C_5(CH_3)_5$ of **3b**], 31.45 [s, *p*-$C(CH_3)_3$ of **3a**], 31.51 [s, *p*-$C(CH_3)_3$ of **3b**], 34.06 s, 34.21 s, 34.33 [s, *o*-$C(CH_3)_3$], 34.60 (m, P–CC–P of **3a**), 34.91 s, 34.93 [s, *p*-$C(CH_3)_3$ of **3a** and **3b**], 38.41 s, 39.04 (d, J_{PC} = 2.8 Hz), 39.90 [s, *o*-$C(CH_3)_3$], 40.10 (dd, J_{PC} = 20.3, 9.9 Hz, P–CC–P of **3b**), 44.61 (dd, J_{PC} = 15.2, 6.0 Hz, P–CC–P of **3b**), 49.41 (t, J_{PC} = 10.6 Hz, P–CC–P of **3a**), 96.78 [s, $C_5(CH_3)_5$ of **3b**], 97.25, [s, $C_5(CH_3)_5$ of **3a**], 122.51 s, 122.55 s, 123.19 (*m* aryl C of **3a** and **3b**), 148.35 (s, *p* aryl C of **3a**), 149.32 (s, *p* aryl C of **3b**), 154.72 s, 155.10 (d, J_{PC} = 1.1 Hz), 155.97 s, 156.70 (d, J_{PC} = 6.6 Hz, *o* aryl C), 170.80 (d, J_{PC} = 2.0 Hz), 174.27 (d, J_{PC} = 3.1 Hz), 178.29 (d, J_{PC} = 19.0 Hz, *N*–CO of **3a** and **3b**), 215.90 (d, J_{PC} = 17.4 Hz, FeCO of **3b**), 216.13 (d, J_{PC} = 12.9 Hz, FeCO of **3a**), 216.71 (d, J_{PC} = 4.2 Hz, FeCO of **3a**), 217.55 (dd, J_{PC} = 8.1, 2.5 Hz, FeCO of **3b**). $^{31}P\{^1H\}$ NMR: δ 126.9 (d, $|^1J_{PP}|$ = 105.2 Hz, P–Fe of **3b**), 107.5 (d, $|^1J_{PP}|$ = 92.4 Hz, P–Fe of **3a**), 15.7 (d, $|^1J_{PP}|$ = 92.4 Hz, P–aryl of **3a**), -19.2 (d, $|^1J_{PP}|$ = 105.2 Hz, P–aryl of **3b**). MS/EI: *m/e* = 650 (M^+ – 2H), 596 (M^+ – 2CO), 554 (1^+), 498 (1^+ – CO).

Anal. Calcd for $C_{34}H_{47}FeNO_4P_2$ (M_r = 651.6): C, 62.68; H, 7.27; N, 2.15; Fe, 8.57. Found: C, 62.94; H, 7.60; N, 2.21; Fe, 7.90.

Reaction of 1 with *N*-Methylmaleimide. Crystaline *N*-methylmaleimide (0.23 g, 2.00 mmol) was added to a vigorously stirred solution of 1.12 g (2.00 mmol) of **1** in 25 mL of benzene. The mixture was warmed to 70–75 °C for 24 h. Then all volatiles were removed in vacuo, and the oily brown residue was solidified by stirring in 50 mL of pentane. The mixture was filtered, and the filtercake was subsequently extracted with pentane until the extracts became colorless. The combined dark red extracts were concentrated to dryness. The orange microcrystalline residue was dissolved in a minimum amount of diethyl ether. One obtained cycloadduct **4** (0.51 g, 38%) as a red crystalline product by fractional crystallization at -28 °C. The solid was a mixture of diastereomers **4a** and **4b** (1:2).

IR (hexane): 1997 vs, 1969 w, 1963 w, 1953 vs [ν(Fe(CO))], 1761 w, 1701 m, 1696 m, 1694 m cm^{-1} [$\nu(CO)_{acyl}$]. IR (Nujol): 1990 vs, 1943 vs, 1941 sh [ν(Fe(CO))], 1759 sh, 1751 w, 1702 w, 1687 s, br, 1683 w cm^{-1} [$\nu(CO)_{acyl}$], 1586 w, 1278 w, 1126 w, 1083 w, 1034 w, 963 w, 592 w cm^{-1}. ^1H NMR: δ 1.34 (s, 9 H, *p*-*t*-Bu of **4a**), 1.40 (s, 9 H, *p*-*t*-Bu of **4b**), 1.48 [s, 15 H, $C_5(CH_3)_5$ of **4a**], 1.52 [s, 15 H, $C_5(CH_3)_5$ of **4b**], 1.55 s, 1.67 s, 1.86 (s, *o*-*t*-Bu of **4a** and **4b**), 2.64 (s, 3 H, NCH_3 of **4b**), 2.74–2.84 (m, 1 H, CH_{ring} of **4b**), 2.88 (s, 3 H, NCH_3 of **4a**), 3.30–3.40 (m, 1 H, CH_{ring} of **4a**), 3.50 and 3.64 (ABXY spectrum, J_{AB} = 7 Hz, J_{AX} = J_{BX} = 3 Hz, J_{AY} = J_{BY} = 0 Hz, 2 H, C_2H_2 ring of **4a**), 7.41 (d, *J* = 2 Hz, 1 H, *m* aryl H of **4b**), 7.45 (d, *J* = 2 Hz, 1 H, *m* aryl H of **4b**), 7.56 (d, *J* = 2 Hz, 1 H, *m* aryl H of **4a**), 7.59 (d, *J* = 2 Hz, 1 H, *m* aryl H of **4a**). $^{13}C\{^1H\}$ NMR: δ 9.23 [s, $C_5(CH_3)_5$ of **4b**], 9.39 [s, $C_5(CH_3)_5$ of **4a**], 24.49 (s, NCH_3 of **4b**), 24.85 (s, NCH_3 of **4a**), 31.48 [s, *p*-$C(CH_3)_3$ of **4a** and **4b**], 33.79 [s, *p*-$C(CH_3)_3$ of **4a** and **4b**], 33.89 (dd, J_{PC} = 34.3, 4.6 Hz, P–CC–P of **4a**), 34.01 s, 34.15 s, 34.28 [s, *o*-$C(CH_3)_3$ of **4a** and **4b**], 38.29 [s, *o*-$C(CH_3)_3$], 38.44 (dd, J_{PC} = 28.8, 8.7 Hz, P–CC–P of **4b**), 39.04 (d, J_{PC} = 2.3 Hz), 39.97 [d, J_{PC} = 2.3 Hz, *o*-$C(CH_3)_3$], 42.40 (dd, J_{PC} = 14.7, 6.0 Hz, P–CC–P of **4b**), 47.97 ("t", J_{PC} = 9.6 Hz, P–CC–P of **4a**), 96.66 [s, $C_5(CH_3)_5$ of **4b**], 97.24 [s, $C_5(CH_3)_5$ of **4a**], 122.29 (s, *m* aryl C of **4b**), 122.52 (s, *m* aryl C of **4a**), 122.63 (s, *m* aryl C of **4a**), 123.22 (s, *m* aryl C of **4b**), 132.20 (dd, J_{PC} = 77.8, 7.4 Hz, i aryl C of **4b**), 148.09 (s, *p* aryl C of **4a**), 148.99 (s, *p* aryl C of **4b**), 154.78 s, 155.14 s, 155.96 s, 156.56 (d, J_{PC} = 5.4 Hz, *o* aryl C of **4a** and **4b**), 173.40 (d, J_{PC} = 3.2 Hz, NCO of **4b**), 177.51 (d, J_{PC} = 18.7 Hz, NCO of **4a**), 179.46 (d, J_{PC} = 2.9 Hz, NCO of **4a**), 180.00 (d, J_{PC} = 14.6 Hz, NCO of **4b**), 215.94 (d, J_{PC} = 17.8 Hz, FeCO of **4b**), 216.00 (d, J_{PC} = 11.0 Hz, FeCO of **4a**), 217.10 (s, FeCO of **4a**), 217.85 (d, J_{PC} = 11.3 Hz, FeCO of **4b**). MS/EI (70 eV): *m/e* 665 (M^+ – H), 609 (M^+ – H – 2CO), 554 (1^+), 498 (1^+ – 2CO), 441 [$(C_5Me_5P{=}P{-}Ar)^+$ – H].

Anal. Calcd for $C_{35}H_{49}NFeO_4P_2$ (M_r = 665.6): C, 63.16; H, 7.42; N, 2.11; Fe 8.39. Found: C, 63.14; H, 7.68; N, 2.13; Fe, 8.42.

X-ray Structure Determination of 4b. The structure of **4b** was determined from a single crystal with the approximate dimensions 0.5 × 0.5 × 0.15 mm^3 by using a SIEMENS R3 m/V four-circle diffractometer (graphite-monochromated Mo Kα radiation, λ = 0.71073 Å). The unit cell dimensions were calculated from 22 centered reflections: *a* = 31.465 (7) Å, *b* = 14.131 (3) Å, *c* = 17.277 (3) Å, β = 94.85 (2)°, V = 7654 (3) $Å^3$, *Z* = 8, d_{calcd} =

---

[3] Weber, L.; Frebel, M.; Boese, R. *Organometallics* **1989**, *8*, 1718.

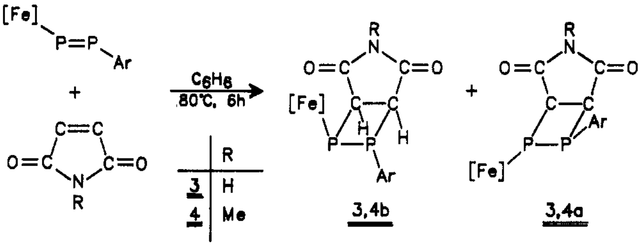
[4] A similar problem, which was met by the addition of a phosphinidene complex to 1,3-dienes, is discussed by Mathey: Mathey, F. *Angew. Chem.* **1987**, *99*, 285; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 275 and references cited therein.

[5] Weber, L.; Reizig, K.; Bungardt, D.; Boese, R. *Organometallics* **1987**, *6*, 110.

1.22 g·cm^{-3}, μ = 5.11 cm^{-1}, space group *C*2/*c*. A total of 7269 reflections were collected at 21 °C to $2\theta_{max}$ = 50°; 4667 reflections were observed ($F_0 > 4\sigma(F_0)$). The structure was solved by direct methods[6] and refined to R = 0.081 and R_w = 0.064 ($w^{-1} = \sigma^2(F) + 0.0001F^2$, 414 parameters) with anisotropic non-hydrogen atoms (except disordered solvent molecule) and riding H atoms in calculated positions (C–H = 0.96 Å, H–C–H = 109.5°). The maximum electron density in the last difference-Fourier map was 0.46 e·Å^{-3}.

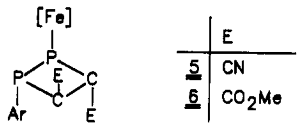
Results

The reaction of equimolar amounts of 1 with maleimide or *N*-methylmaleimide in boiling benzene over a 24-h period leads to red crystalline solid **3** or **4** in 38% yield. Both products proved to be 1:2 mixtures of the two isomers **3a** and **3b**, and **4a** and **4b**, respectively, which result from the endo or exo [2 + 2] cycloaddition of diphosphene 1 to the olefinic double bond of the maleimides.



Until now it was impossible to separate the diastereomeric mixtures by, e.g., fractional crystallization or chromatography. The $^{31}P\{^1H\}$ NMR spectrum of **3** displays four doublets, which are conveniently assigned to the minor isomer **3a** (δ 107.5 and 15.7, $^1J_{PP}$ = 92.3 Hz) and the major isomer **3b** (δ 126.9 and 19.2, $^1J_{PP}$ = 105.0 Hz). Both are present in a 1:2 ratio.

From the 1,2-diphosphetanes **5** and **6** similar ^{31}P NMR data were obtained (for **5**, δ 128.2 d, -12.7 d, $^1J_{PP}$ = 113.0 Hz; for **6**, δ 124.5 d, -22.8 d, J_{PP} = 125.4 Hz).[7]



The ^1H NMR spectrum of **3** shows for the two protons at the four-membered ring of both isomers multiplets at δ 2.82–2.91 and 3.40–3.63. The former group is tentatively assigned to one ring proton of the major isomer. The carbon atoms of the 1,2-diphosphetane ring are observed as doublets of doublets at δ 40.10 (J_{PC} = 20.3, 9.9 Hz) and 44.61 (J_{PC} = 15.2, 6.0 Hz) for **3b** and as poorly resolved multiplets at δ 34.60 and 49.41 for **3a**. The carbonyl groups of the imide ring of both isomers give rise to doublets at δ 170.8 (J_{PC} = 2.0 Hz), 174.27 (J_{PC} = 3.1 Hz), and 178.29 (J_{PC} = 19.0 Hz). The ^{13}C nuclei of the terminal carbonyl ligands of **3b** resonate at δ 215.90 (d, J_{PC} = 17.4 Hz) and 217.55 (dd, J_{PC} = 8.1, 2.5 Hz) whereas the signals of **3a** are encountered at δ 216.13 (d, J_{PC} = 12.9 Hz), and 216.71 (d, J_{PC} = 4.2 Hz). The $Fe(CO)_2$ group is revealed in the IR spectrum (cyclopentane solution) as two intense ν(CO) bands at 1997 and 1952 cm^{-1}. There is an obvious long-wave shift in going from 1 [ν(CO) = 2005, 1956 cm^{-1}] to **3**. In diphosphetane **5**, the stretching modes of the carbonyl ligands were registered at 2008 and 1958 cm^{-1}. Strong absorptions at 1725 and 1705 cm^{-1} and medium-intensity bands at 1760 and 1739 cm^{-1} are assigned to the carbonyl stretches of the imide functionality.

The spectra of **4** reveal a comparable situation. Again doublets in the ^{31}P NMR spectrum at δ 107.3 and 17.5 ($^1J_{PP}$ = 91.1 Hz) and δ 118.8 and -10.3 ($^1J_{PP}$ = 103.6 Hz) are caused by the diastereoisomers **4a** and **4b** (ratio 1:2). The same ratio of intensities is encountered in the ^1H NMR spectrum at δ 2.88 (**4a**) and 2.64 (**4b**). The protons on the four-membered ring of the major isomer are observed as multiplets at δ 2.74–2.84 and 3.30–3.40. The AB part of an ABX spectrum at $\delta(H_A)$ = 3.50 and $\delta(H_B)$ = 3.64 (J_{AB} = 7 Hz, $J_{AX} = J_{BX}$ = 3 Hz) is due to corresponding protons of the minor isomer **4a**. The carbon atoms of the diphosphetane ring in **4a** are assigned to signals at δ 33.89 (dd, J_{PC} = 34.3, 4.6 Hz) and δ 47.94 ("t", J_{PC} = 9.6 Hz), whereas resonances at 38.44 (dd, J_{PC} = 28.8, 8.7 Hz) and 42.40 (dd, J_{PC} = 14.7, 6.0 Hz) correspond to the ring carbons in **4b**. These absorptions may be compared with those for the diphosphetane **6**, where a doublet of doublets at δ 37.5 (J_{PC} = 35.8, 27.1 Hz), and a triplet at 49.8 (J_{PC} = 15.1 Hz) are measured for the ring carbons.[7] The discrimination between the carbonyls of the imino functions of both isomers [for **4a**, δ 177.51 (d, J_{PC} = 18.7 Hz) and 179.46 (d, J_{PC} = 2.9 Hz); for **4b**, δ 173.40 (d, J_{PC} = 3.2 Hz) and 180.00 (d, J_{PC} = 14.6 Hz)] is possible, and the same is true for terminal carbonyl ligands [for **4a**, δ 216.0 (J_{PC} = 11.0 Hz, 217.1 s; for **4b**, δ 215.94 (d, J_{PC} = 17.8 Hz)]. In **6** doublets at δ 216.2 (J_{PC} = 14.8 Hz) and 216.8 (J_{PC} = 4.1 Hz) are assigned to the ^{13}C nuclei of the carbonyl ligands.

X-ray Structure Analysis of 4b. The X-ray structure analysis of **4**, presumably the major isomer **4b**, confirms the conclusion derived from analyses and spectroscopic data. The result of the structural determinations are shown in Figure 1. Positional parameters for the complex are given in Table I, and derived distances, angles, and anisotropic displacement coefficients are presented in Tables II–IV. The analysis shows the presence of a 4,5-diphospha-2-azabicyclo[3.2.0]hepta-1,3-dione system linked to the metal through a Fe–P single bond [2.319 (2) Å]. This distance falls in the range of Fe–P bonds in low-valent carbonyl iron compounds (2.11–2.39 Å).[8] It is markedly longer than the Fe–P linkage in 1 [2.260 (1) Å][5] and even longer than that in diphosphetane **5** [2.270 (1) Å].[7] Obviously this bond elongation is caused by steric interactions of the organometallic fragment with the succinimide part of the molecule. The organophosphorus ligand could be regarded as one leg in a distorted three-legged piano stool arrangement. The three angles the ligand forms with the metal center are P(1)–Fe–C(1) = 97.5 (2)°, C(1)–Fe–C(2) = 90.7 (3)°, and P(1)–Fe–C(2) = 91.4 (2)°. The obtuse angle P(1)–Fe–C(1) again is a result of steric interactions within the ligand sphere at the iron atom. Two legs of the piano stool are represented by terminal, nearly linear, carbonyl groups. The cyclopentadienyl ring is attached to the metal via Fe–C bonds of 2.122 Å (average). The iron atom is located 1.742 Å above the center of the ring. The most interesting structural feature of **4b** is the geometry of the bicyclic ligand, which is attached to the iron via phosphorus atom P(1). The ligand is composed of a nearly planar 1,2-diphosphetane (mean deviation from least-squares plane through the atoms P(1), P(2), C(5), and C(6) = 0.032 Å), which is fused to a planar succinimide ring

---

[6] SIEMENS-SHELXTL-Plus program package, written by G. M. Sheldrick, University of Göttingen; the program uses scattering factors from: *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

[7] Weber, L.; Frebel, M.; Boese, R. *Chem. Ber.* **1990**, *123*, 733.

[8] (a) Knoll, K.; Huttner, G.; Wasiucionek, M.; Zsolnai, L. *Angew. Chem.* **1984**, *96*, 708; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 739. (b) Lal De, R.; Vahrenkamp, H. *Z. Naturforsch. B.* **1986**, *41*, 273. (c) Arif, A. M.; Cowley, A. H.; Pakulsky, M. *J. Am. Chem. Soc.* **1985**, *107*, 2553. (d) Huttner, G.; Mohr, G.; Friedrich, P.; Schmid, H. G. *J. Organomet. Chem.* **1978**, *160*, 59. (e) Williams, G. D.; Geoffroy, G. L.; Whittle, R. R.; Rheingold, A. L. *J. Am. Chem. Soc.* **1985**, *107*, 729.

Table I. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) of 4b

	x	*y*	*z*	*U*(eq)[a]
Fe	3204 (1)	1456 (1)	1877 (1)	40 (1)
P(1)	3335 (1)	42 (1)	2536 (1)	42 (1)
P(2)	3734 (1)	−853 (1)	1796 (1)	44 (1)
N	2560 (1)	−1019 (3)	1032 (3)	49 (2)
C(1)	3042 (2)	972 (4)	967 (3)	51 (2)
O(1)	2942 (2)	742 (3)	347 (2)	84 (2)
C(2)	3734 (2)	1513 (4)	1633 (3)	55 (2)
O(2)	4070 (2)	1602 (3)	1435 (3)	85 (2)
C(3)	2527 (2)	−735 (4)	1782 (3)	48 (2)
O(3)	2207 (1)	−375 (3)	2011 (2)	62 (2)
C(4)	2941 (2)	−1453 (4)	919 (3)	51 (2)
O(4)	3031 (1)	−1754 (3)	307 (2)	75 (2)
C(5)	3201 (2)	−1503 (4)	1692 (3)	47 (2)
C(6)	2936 (2)	−950 (4)	2242 (3)	44 (2)
C(7)	2225 (2)	−897 (5)	402 (3)	68 (2)
C(8)	2797 (2)	1816 (4)	2767 (3)	44 (2)
C(9)	3198 (2)	2285 (4)	2895 (3)	45 (2)
C(10)	3247 (2)	2880 (4)	2242 (3)	49 (2)
C(11)	2883 (2)	2765 (4)	1708 (3)	47 (2)
C(12)	2605 (2)	2092 (4)	2034 (3)	45 (2)
C(13)	2597 (2)	1222 (4)	3353 (3)	59 (2)
C(14)	3495 (2)	2233 (5)	3620 (3)	66 (2)
C(15)	3604 (2)	3573 (4)	2173 (4)	71 (3)
C(16)	2791 (2)	3309 (4)	974 (3)	72 (3)
C(17)	2175 (2)	1827 (4)	1678 (3)	64 (2)
C(18)	4010 (2)	−2689 (4)	2270 (3)	43 (2)
C(19)	4031 (2)	−3370 (4)	2857 (3)	48 (2)
C(20)	4090 (2)	−3161 (4)	3631 (3)	48 (2)
C(21)	4176 (2)	−2227 (4)	3814 (3)	56 (2)
C(22)	4157 (2)	−1498 (4)	3273 (3)	51 (2)
C(23)	4009 (2)	−1722 (3)	2491 (3)	41 (2)
C(24)	4033 (2)	−3094 (4)	1439 (3)	54 (2)
C(25)	4080 (2)	−2382 (4)	789 (3)	64 (2)
C(26)	3651 (2)	−3742 (4)	1189 (4)	69 (3)
C(27)	4439 (2)	−3706 (5)	1468 (4)	85 (3)
C(28)	4102 (2)	−3925 (4)	4268 (3)	57 (2)
C(29)	3900 (3)	−4856 (5)	3961 (5)	125 (4)
C(30)	4541 (2)	−4089 (7)	4571 (5)	165 (5)
C(31)	3842 (3)	−3634 (6)	4907 (5)	144 (5)
C(32)	4363 (2)	−551 (4)	3562 (4)	65 (2)
C(33)	4832 (2)	−801 (5)	3834 (4)	96 (3)
C(34)	4146 (2)	−149 (5)	4249 (4)	91 (3)
C(35)	4379 (2)	211 (4)	2941 (4)	74 (3)
C(36)[b]	−62 (12)	1788 (37)	6719 (23)	198 (16)
C(37)[b]	265 (8)	1712 (19)	7231 (16)	140 (9)
C(38)[b]	34 (14)	1304 (21)	7128 (18)	190 (14)
C(39)[b]	209 (7)	2306 (18)	6073 (14)	148 (8)
C(40)[b]	219 (16)	1800 (43)	6513 (32)	129 (17)
C(41)[b]	0	2248 (49)	7500	143 (22)
C(42)[b]	78 (20)	2224 (37)	6655 (32)	118 (17)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor. [b] Positions of the disordered solvent molecule with occupancy factors between 0.125 and 0.5.

Table II. Selected Bond Lengths (Å) for 4b[a]

Fe–P(1)	2.319 (2)	Fe–C(1)	1.751 (6)
Fe–C(2)	1.754 (7)	Fe–C(8)	2.144 (6)
Fe–C(9)	2.115 (5)	Fe–C(10)	2.109 (5)
Fe–C(11)	2.115 (5)	Fe–C(12)	2.127 (5)
P(1)–P(2)	2.255 (2)	P(1)–C(6)	1.921 (5)
P(2)–C(5)	1.906 (5)	P(2)–C(23)	1.877 (5)
N–C(3)	1.369 (8)	N–C(4)	1.375 (7)
N–C(7)	1.460 (7)	C(1)–O(1)	1.137 (7)
C(2)–O(2)	1.148 (8)	C(3)–O(3)	1.224 (7)
C(4)–O(4)	1.197 (7)	C(3)–C(6)	1.485 (7)
C(4)–C(5)	1.508 (7)	C(5)–C(6)	1.531 (7)
Cp*–Fe	1.742 (6)		

[a] Cp* describes the center of the ring.

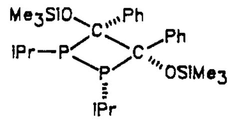
Table III. Selected Bond and Torsion Angles (deg) for 4b

Bond Angles			
P(1)–Fe–C(1)	97.5 (2)	P(1)–Fe–C(2)	91.4 (2)
C(1)–Fe–C(2)	90.7 (3)	Fe–P(1)–P(2)	106.8 (1)
Fe–P(1)–C(6)	114.5 (2)	P(1)–P(2)–C(5)	78.2 (2)
P(2)–P(1)–C(6)	79.8 (2)	P(1)–P(2)–(23)	104.6 (2)
C(5)–P(2)–C(23)	95.7 (2)	C(3)–N–C(4)	113.7 (4)
C(3)–N–C(7)	124.3 (5)	C(4)–N–C(7)	122.0 (5)
Fe–C(1)–O(1)	173.4 (5)	Fe–C(2)–O(2)	174.9 (5)
N–C(3)–O(3)	123.9 (5)	N–C(3)–C(6)	108.4 (5)
O(3)–C(3)–C(6)	127.7 (5)	N–C(4)–O(4)	124.0 (5)
N–C(4)–C(5)	108.1 (5)	O(4)–C(4)–C(5)	127.9 (5)
P(2)–C(5)–C(4)	117.9 (4)	P(2)–C(5)–C(6)	102.5 (3)
P(1)–C(6)–C(3)	120.6 (4)	P(1)–C(6)–C(5)	99.1 (3)
C(3)–C(6)–C(5)	105.4 (4)	C(4)–C(5)–C(6)	103.9 (4)
Cp*–Fe–P(1)	119.1 (3)	CP*–Fe–C(1)	125.4 (3)
Cp*–Fe–C(2)	124.2 (3)		

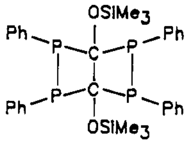
Torsion Angles	
Fe–P(1)–P(2)–C(5)	−109.3
Fe–P(1)–P(2)–C(23)	157.8
C(6)–P(1)–P(2)–C(5)	3.3
C(6)–P(1)–P(2)–C(23)	−89.5
P(1)–P(2)–C(5)–C(4)	109.2
P(1)–P(2)–C(5)–C(6)	−4.2
C(23)–P(2)–C(5)–C(4)	−147.0
C(23)–P(2)–C(5)–C(6)	99.6
Fe–P(1)–C(6)–C(3)	−14.3
Fe–P(1)–C(6)–C(5)	99.8
P(2)–P(1)–C(6)–C(3)	−118.2
P(2)–P(1)–C(6)–C(5)	−4.1
P(2)–C(5)–C(6)–P(1)	4.9
P(2)–C(5)–C(6)–C(3)	130.3
C(4)–C(5)–C(6)–P(1)	−118.4
C(4)–C(5)–C(6)–C(3)	7.0

[a] Cp* describes the center of the ring.

(mean deviation from least-squares plane through the atoms N, C(3), C(4), C(5), and C(6) = 0.028 Å) via the carbon atoms C(5) and C(6) [C(5)–C(6) = 1.531 (7) Å]. Both planes enclose a dihedral angle of 123.7°. This is an contrast to the tilted 1,2-diphosphetane moiety in **5** (dihedral angle 132.6°).[7] The organoiron fragment is attached to the phosphorus atom P(1) at the concave face (endo) of the bicyclic ligand, whereas the supermesityl substituent takes the convex (exo) position. The *E* configuration at the P–P building block of **1** has been maintained during the cycloaddition. The atoms Fe, P(1), P(2), and C(23), however, are no longer arranged in the same plane, as is indicated by the torsion angle Fe–P(1)–P(2)–C(23) = 157.8°. The P(1)–P(2) bond distance [2.255 (2) Å] and the exocyclic P(2)–C(23) bond distance [1.877 (5) Å] correspond well with the standard values of P–P and P–C single bonds (2.22[9] and 1.85 Å,[10] respectively). Compared with this, the endocyclic P–C distances [1.906 (5) and 1.921 (5) Å, respectively] are significantly longer. In the 1,2-diphosphetanes **5**, **7**, and **8** long endocyclic C–P bonds were also encountered [**5**, 1.889 (3) and 1.934 (3) Å; **7**, 1.918 (3) and 1.930 (3) Å,[11] and **8**, 1.887 (6) and 1.950 (6) Å[12]]. P–P bond lengths in these compounds are as follows: **5**, 2.249 (1) Å; **7**, 2.204 (1) Å; **8**, 2.228 (2) Å.



7



8

The endocyclic bond angles at the P atoms in **4b** [C(6)–

---

(9) (a) Tebbe, K. F. *Z. Anorg. Allg. Chem.* **1980**, *468*, 202. (b) Bart, J. C. J. *Acta Crystallogr., Sect. B* **1969**, *25*, 762.

(10) Corbridge, D. E. C. *The Structural Chemistry of Phosphorus*; Elsevier Scientific Publishing Co.: Amsterdam, 1974; p 393.

(11) Becker, G.; Becker, W.; Mendt, O. *Phosphorus Sulfur* **1983**, *14*, 267.

(12) Appel, R.; Barth, V.; Halstenberg, M.; Huttner, G.; Seyerl, J. *Angew. Chem.* **1979**, *91*, 935; *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 872.

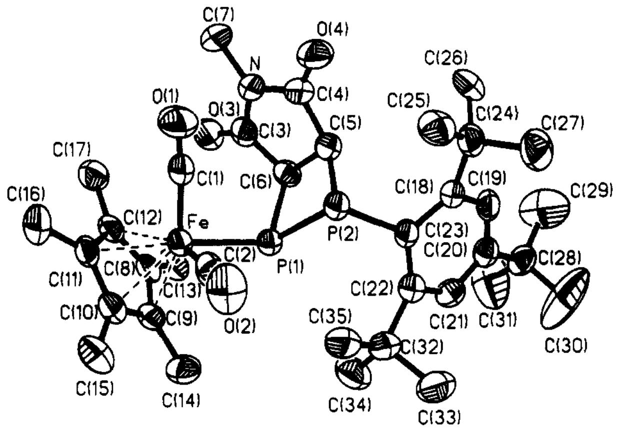


Figure 1. Molecular structure of **4b**.

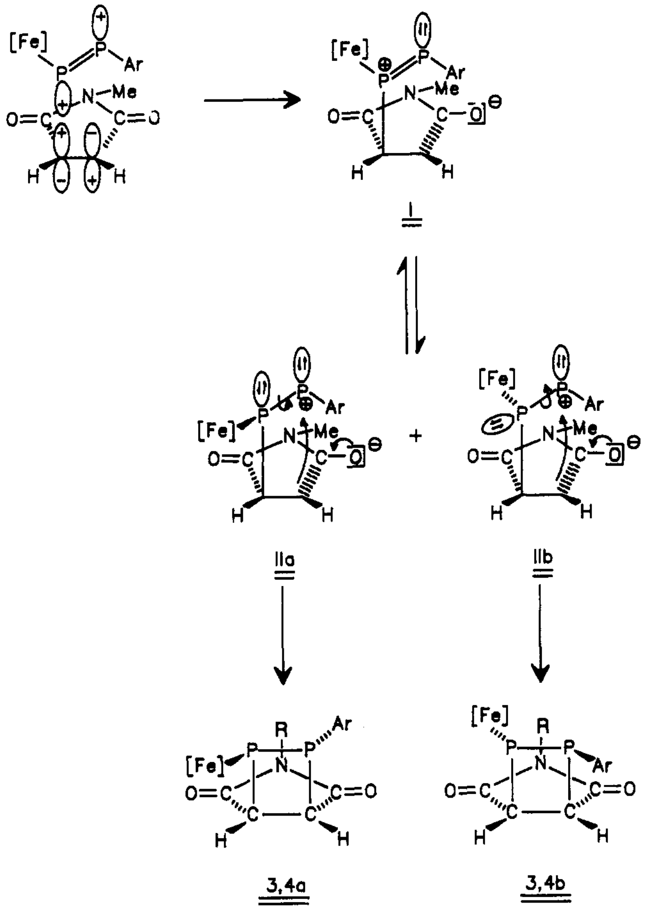
Table IV. Anisotropic Displacement Coefficients ($Å^2 \times 10^3$) for 4b[a]

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe	47 (1)	32 (1)	41 (1)	2 (1)	1 (1)	1 (1)
P(1)	50 (1)	36 (1)	39 (1)	3 (1)	-2 (1)	0 (1)
P(2)	50 (1)	39 (1)	42 (1)	6 (1)	-1 (1)	2 (1)
N	46 (3)	50 (3)	50 (3)	9 (2)	-5 (2)	-7 (2)
C(1)	64 (4)	37 (3)	50 (4)	7 (3)	-5 (3)	4 (3)
O(1)	127 (4)	75 (3)	46 (3)	3 (3)	-12 (3)	-11 (3)
C(2)	71 (4)	36 (3)	59 (4)	2 (3)	8 (3)	10 (3)
O(2)	66 (3)	78 (3)	115 (4)	0 (3)	33 (3)	21 (3)
C(3)	47 (4)	32 (3)	65 (4)	-9 (3)	4 (3)	5 (3)
O(3)	48 (3)	55 (3)	82 (3)	-1 (2)	7 (2)	-7 (2)
C(4)	55 (4)	47 (3)	49 (4)	-2 (3)	-7 (3)	-6 (3)
O(4)	72 (3)	96 (4)	54 (3)	20 (3)	-10 (2)	-25 (3)
C(5)	55 (3)	41 (3)	43 (3)	3 (3)	-3 (3)	2 (3)
C(6)	50 (3)	36 (3)	46 (3)	-7 (3)	6 (3)	0 (3)
C(7)	59 (4)	74 (4)	66 (4)	12 (3)	-24 (3)	-13 (4)
C(8)	50 (4)	32 (3)	51 (4)	5 (3)	10 (3)	-7 (3)
C(9)	50 (3)	39 (3)	45 (3)	3 (3)	4 (3)	-12 (3)
C(10)	53 (4)	37 (3)	59 (4)	2 (3)	9 (3)	-7 (3)
C(11)	55 (4)	33 (3)	52 (4)	12 (3)	5 (3)	-3 (3)
C(12)	44 (3)	36 (3)	55 (4)	5 (3)	3 (3)	-11 (3)
C(13)	71 (4)	45 (4)	63 (4)	-2 (3)	21 (3)	-6 (3)
C(14)	72 (4)	75 (5)	50 (4)	3 (4)	-8 (3)	-14 (3)
C(15)	84 (5)	43 (4)	88 (5)	-12 (4)	12 (4)	-4 (4)
C(16)	87 (5)	51 (4)	76 (5)	15 (3)	-4 (4)	14 (3)
C(17)	54 (4)	53 (4)	83 (5)	-1 (3)	-3 (3)	-10 (3)
C(18)	43 (3)	41 (3)	45 (3)	9 (3)	-3 (3)	-2 (3)
C(19)	53 (3)	38 (3)	53 (4)	12 (3)	3 (3)	4 (3)
C(20)	50 (4)	44 (3)	51 (4)	5 (3)	2 (3)	9 (3)
C(21)	65 (4)	60 (4)	40 (3)	7 (3)	-12 (3)	4 (3)
C(22)	54 (4)	46 (3)	52 (4)	5 (3)	-4 (3)	-1 (3)
C(23)	43 (3)	39 (3)	42 (3)	8 (2)	0 (3)	2 (2)
C(24)	60 (4)	54 (4)	48 (4)	18 (3)	5 (3)	-4 (3)
C(25)	76 (4)	69 (4)	48 (4)	2 (4)	14 (3)	-6 (3)
C(26)	88 (5)	43 (4)	74 (5)	3 (3)	0 (4)	-21 (3)
C(27)	87 (5)	98 (6)	71 (5)	39 (4)	12 (4)	-16 (4)
C(28)	57 (4)	57 (4)	55 (4)	2 (3)	-6 (3)	16 (3)
C(29)	168 (8)	100 (7)	102 (6)	-51 (6)	-21 (6)	46 (5)
C(30)	82 (6)	190 (10)	216 (11)	-10 (6)	-27 (6)	165 (9)
C(31)	224 (11)	113 (7)	107 (7)	56 (8)	76 (7)	55 (6)
C(32)	69 (4)	56 (4)	66 (4)	-1 (3)	-21 (3)	-6 (3)
C(33)	91 (5)	69 (5)	119 (6)	-12 (4)	-48 (5)	6 (5)
C(34)	138 (7)	62 (5)	67 (5)	9 (4)	-21 (5)	-18 (4)
C(35)	72 (5)	57 (4)	88 (5)	-11 (3)	-21 (4)	-4 (4)

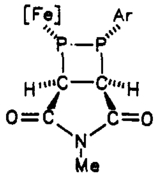
[a] The anisotropic displacement exponent takes the form $-2\pi^2(h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12})$.

P(1)–P(2) = 79.8 (2), P(1)–P(2)–C(5) = 78.2 (2)°] are significantly smaller than those at the carbon atoms [C(6)–C(5)–P(2) = 102.5 (3)°, P(1)–C(6)–C(5) = 99.1 (3)°]. This situation may be compared with the respective angles in 7 [at P, 77.2 (2) and 76.9 (2)°; at C, 94.2 (3) and 93.9 (3)°] and 8 [at P, 77.3 (2) and 76.4 (2); at C, 93.8 (4) and 96.8 (4)°].

Discussion of the Reaction Mechanism. A [2 + 2] cycloaddition is known to be a nonconcerted two-step process.[13] The HOMO of **1** is mainly represented by the lone pair at the metalated phosphorus atom. In the first step of the reaction, this orbital interacts with the π^* MO of the carbon–carbon double bond to give the zwitterionic adduct I. Pyramidalization of the metalated phosphorus leads to zwitterions IIa and IIb. The positive charge herein is centered at the arylated phosphorus as is known from studies of planar phosphenium ions.[14] Rotation around the C–P single bond and attack of the carbanion at the phosphenium center furnishes both diastereoisomers of **3** and **4**. Thereby the trans orientation of the bulky aryl group and the metal complex fragment is maintained as it is the case in all our cycloadducts of **1**. Steric hindrance between the bulky supermesityl group in the concave position of the bicyclic system may be one of the reasons to favor diastereoisomers **3b** and **4b** over **3a** and **4a**.



Principally, it is conceivable that the other isomer might have structure **3a′** or **4a′** with the two bulky substituents in the cis position and trans orientated to the fused imino ring.



3,4a′

This would mean large exocyclic FePP and $PPC_{(aryl)}$ angles

---

(13) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; John Wiley & Sons: Chichester, England, 1976.

(14) For a review, see: Cowley, A. H.; Kemp, R. A. *Chem. Rev.* **1985**, *85*, 367 and references therein.

and an increased $^1J_{PP}$ coupling as compared to the other isomer. This, however, is not the case, and therefore structure **3a′** and **4a′** are ruled out.

Supplementary Material Available: Tables of crystal data, atomic coordinates and equivalent isotropic displacement coefficients, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom parameters (10 pages); a table of observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

Platinum(IV)–Azobenzene Cyclometalation Products and Related Species

Surajit Chattopadhyay, Chittaranjan Sinha, Partha Basu, and Animesh Chakravorty*

Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Calcutta 700032, India

Received August 14, 1990

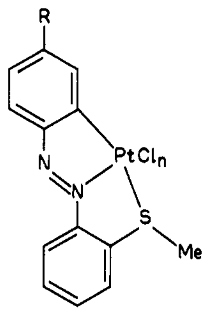
The first platinum(IV) cyclometalates of azobenzene, $Pt^{IV}(RL)Cl_3$ (R = H, Me), have been synthesized by oxidation of $Pt^{II}(RL)Cl$ by chlorine or *m*-chloroperbenzoic acid (Pt(RL) = cycloplatinated 2-(methylthio)azobenzene fragment). The X-ray structures of $Pt(MeL)Cl_3$ and Pt(MeL)Cl are reported. In both cases the organic moiety acts as a planar tridentate (C,N,S) ligand and the lattice consists of loose dimers held by nonbonded S···S interactions. The Pt–C distances are equal in the two molecules, but the other metal–ligand distances are longer (e.g., Pt–S by ~0.09 Å) in $Pt(MeL)Cl_3$. Weakening of back-bonding upon metal oxidation may be one of the reasons. In ^1H NMR spectra, the ^3J coupling constant between ^{195}Pt and ^1H(SMe) increases from 12.3 Hz in $Pt(MeL)Cl_3$ to 20.1 Hz in Pt(MeL)Cl, in accord with the increase in 6s character of the metal hybrid orbitals. The complexes Pt(MeL)Cl and Pd(MeL)Cl are isomorphous, with very similar bond parameters. However, chlorine and mCPBA, which oxidize the metal in Pt(RL)Cl, attack the Pd–C bond (in effect the coordinated ligand is attacked) in Pd(RL)Cl, leaving the metal oxidation state unchanged. The reactivity difference corresponds to the nucleophilicity orders $Pt^{II} \gg Pd^{II}$ and Pd–C ≫ Pt–C. Crystal data for $Pt(MeL)Cl_3$: space group $P2_1/n$; $a = 7.436$ (2) Å, $b = 18.613$ (4) Å, $c = 12.335$ (2) Å, $\beta = 104.66$ (2)°; $Z = 4$, $V = 1651.6$ (6) Å^3. Crystal data for Pt(MeL)Cl: space group $P\bar{1}$; $a = 7.421$ (5) Å, $b = 8.830$ (5) Å; $c = 11.083$ (6) Å, $\alpha = 105.44$ (4)°, $\beta = 92.05$ (5)°, $\gamma = 97.16$ (5)°; $Z = 2$, $V = 692.7$ (7) Å^3. Crystal data for Pd(MeL)Cl: space group $P\bar{1}$; $a = 7.424$ (3) Å, $b = 8.833$ (4) Å, $c = 11.127$ (4) Å, $\alpha = 105.44$ (3)°, $\beta = 93.26$ (3)°, $\gamma = 96.81$ (3)°; $Z = 2$, $V = 695.4$ (5) Å^3.

Introduction

Platinum(IV) organometallics containing Pt–C(aryl) bonds are rare.[1] In particular, ortho-metalated platinum(IV) species were virtually unknown until very recently and current knowledge is limited to just a few compounds synthesized by oxidative addition of halogens or halocarbons to platinum(II) precursors.[2-6] The platinum(II)–azobenzene system is as old as ortho metalation,[7] but platinum(IV) analogues remain unknown. Herein we describe the first examples of such species incorporating 2-(methylthio)azobenzene and having the coordination sphere $Pt(C,N,S)Cl_3$, which have been characterized by X-ray crystallography. Synthesis involves the treatment of the bivalent precursor Pt(C,N,S)Cl with chlorine or *m*-chloroperbenzoic acid in chlorocarbon solvents. These oxidants also react with Pd(C,N,S)Cl,[8] transforming the ligand without affecting the metal oxidation state. The origin of this reactivity divergence is examined. Structure determination has not revealed the presence of any gross mismatch between Pt(C,N,S)Cl and Pd(C,N,S)Cl in molecular shape or dimension.

Results and Discussion

Synthesis and Interconversion. The ortho-metalated fragment of interest in the present work is abbreviated Pt(RL). Cyclometalation of 2-(methylthio)azobenzenes by K_2PtCl_4 proceeds smoothly in hot aqueous ethanol, affording the brown Pt(RL)Cl (**1a**) in excellent yields. Orange-yellow $Pt(RL)Cl_3$ (**1b**) is isolated by oxidizing Pt(RL)Cl with chlorine in acetonitrile solution or, less efficiently, with *m*-chloroperbenzoic acid (mCPBA) in chlorocarbon solvents (vide infra).



R = H , Me
$Pt(RL)Cl_n$
1a , n=1
1b , n=3

The reduction of $Pt(RL)Cl_3$ back to Pt(RL)Cl can be achieved in several ways. In acetonitrile solution $Pt(MeL)Cl_3$ displays an irreversible cyclic voltammetric metal

---

[1] Hartley, F. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1982; Vol. 6, Chapter 39.

[2] (a) von Beek, J. A. M.; van Koten, G.; Smeets, W. J. J.; Spek, A. L. *J. Am. Chem. Soc.* **1986**, *108*, 5010. (b) van Koten, G.; Terheijden, J.; von Beek, J. A. M.; Ooyevaar, I. C. M. W.; Muller, F.; Stam, C. H. *Organometallics* **1990**, *9*, 903.

[3] (a) Chassot, L.; von Zelewsky, A.; Sandrini, D.; Maestri, M.; Balzani, V. *J. Am. Chem. Soc.* **1986**, *108*, 6084. (b) Sandrini, D.; Maestri, M.; Balzani, V.; Chassot, L.; von Zelewsky, A. *J. Am. Chem. Soc.* **1987**, *109*, 7720. (c) Chassot, L.; von Zelewsky, A. *Helv. Chim. Acta* **1986**, *69*, 1855.

[4] Deuschel, C. C.; von Zelewsky, A. *Inorg. Chem.* **1987**, *26*, 3354.

[5] Wehman, E.; van Koten, G.; Knaap, C. T.; Ossor, H.; Pfeffer, M.; Spek, A. L. *Inorg. Chem.* **1988**, *27*, 4409.

[6] Anderson, C. M.; Puddephatt, R. J.; Ferguson, G.; Lough, A. J. *J. Chem. Soc., Chem. Commun.* **1989**, 1297.

[7] Cope, A. C.; Siekman, R. W. *J. Am. Chem. Soc.* **1965**, *87*, 3272.

[8] Mahapatra, A. K.; Bandyopadhyay, D.; Bandyopadhyay, P.; Chakravorty, A. *Inorg. Chem.* **1986**, *25*, 2214.

0276-7333/91/2310-1135$02.50/0