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Carbanions α to a Sulfoxide Moiety: Structure of the Naked Form and the Metalation Reaction

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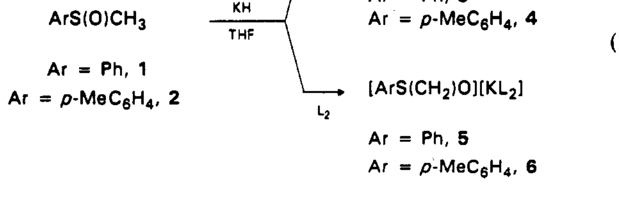
Summary: Deprotonation of methyl sulfoxides $ArSOCH_3$ *[Ar = Ph* (**1**), *p*-MeC_6H_4 (**2**)*] using KH, followed by the treatment with 18-crown-6* (L_1) *or kryptofix-2.2.2* (L_2), *led to the isolation of the corresponding contact-ions* $[ArS(CH_2)O\cdots KL_1]$ *(Ar = Ph,* **3***; Ar = p*-MeC_6H_4, **4**) *and naked forms* $[ArS(O)CH_2]^-[KL_2]^+$ *(Ar = Ph,* **5***; Ar = p*-MeC_6H_4, **6**)*. Reaction of* **4** *with* $[Cr(CO)_5(THF)]$ *led to the C–metal bonded form in* $[ArS(O)CH_2Cr(CO)_5\cdots KL_1]$ (**7**) *(Ar = p*-MeC_6H_4*). Reaction of the deprotonated forms of* **1** *and* **2** *with cis*-$(PPh_3)_2PdCl_2$ *formed the corresponding [trans*-$(PPh_3)_2PD(Cl)(CH_2SOAr)$*]* (**8**, **9**)*. In all reactions involving optically pure* **2** *as starting material we observed a loss of chirality of the α-sulfenyl anion. Complex* **8** *is active in migratory insertion reactions, as reported in the case of* Bu^tNC *leading to a double insertion of the isocyanide functionality, giving* $[(PPh_3)(Bu^tNC)(Cl)PdC(NBu^t)C(HNBu^t){=}CHS(O)Ph]$ (**11**).

Carbanions α to a sulfoxide moiety have been important in recent years for developing new methods for making C–C bonds.[1] In addition to the facility by which a chiral sulfoxide functionality can be introduced in a molecule, the corresponding carbanions become an important synthon in asymmetric synthesis.[2]

This report had as a major goal to reveal some fundamental structural aspects of a carbanion α to a sulfoxide group in its naked or contact-ion form and to control its chemistry by the use of a transition metal.

The deprotonation of **1** and **2** as $R(+)$ pure enantiomers was carried out with KH in THF. Then the solution was treated with either 18-crown-6 (L_1) or kryptofix-2.2.2 (L_2). The solids recrystallized from Et_2O gave (ca. 80%) crystals of **3**–**6**.[3] In the cases of **4** and **6**, the racemic forms were obtained.



(1)

Complexes **3**–**6** have been fully characterized including X-ray analyses on **3**[4] and **5**. The former one is reported in Figure 1 showing the α-sulfenyl$\cdots$K interaction. A self-resolution was observed in the solid state with an ee of 87:13. The most abundant enantiomer is shown in Figure 1, with a selected list of structural parameters. Very similar structural parameters have been found for the naked form **5**. Such data can be compared with those for the lithiated dimeric form $[\{PhCH(Me)S(O)Ph\}_2(\mu\text{-}LiTMEDA)_2]$.[5] The S–O and S–C bond distances are S1–O7 = 1.521 (7) (complex **3**) vs 1.58 (1) Å and S1–C27 = 1.664 (16) (complex **3**) vs 1.63 (1) Å, respectively. The O$\cdots$K interaction, weaker than the O$\cdots$Li one, is probably responsible for the observed differences in S–O and S–C bond distances.

The reaction with oxophilic metals such as Ti^{IV} and Zr^{IV} in various complexes did not lead to any of the M–O

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(1) Krohn, K. In *Organic Synthesis Highlights*; Mulzer, J., Altenbach, H. J., Braun, M., Krohn, K., Reissig, H. U., Eds.; VCH: Weinheim, Germany, 1990; and references therein.

(2) Trost, B. A. *Chem. Rev.* **1978,** *78,* 363. Solladié, G. In *Asymmetric Synthesis*; Morrison, J. D., Ed., Academic: New York, 1983; Vol. 2, p 157. Posner, G. H. In *Asymmetric Synthesis*; Morrison, J. D., Ed., Academic: New York, 1983; Vol. 2, p 225. Solladié, G. *Synthesis* **1981,** 185. Solladié, G. *Pure Appl. Chem.* **1988,** *60,* 1699.

(3) Procedures for **3–6** are as follows. **3**: Melted **1** (2.23 g, 15.9 mmol) was added with a syringe to a THF (50 mL) suspension of KH (0.67 g, 16.7 mmol) and the solution stirred overnight. Excess KH was filtered off and the crown ether added. The solvent was evaporated and the yellow microcrystalline solid redissolved in ether (50 mL), filtered, and dried (87%). Anal. Calcd for $C_{19}H_{31}KO_7S$: C, 51.56; H, 7.06. Found: C, 51.52; H, 7.11. ^1H NMR (C_6D_6): δ 2.50 (s, $=CH_2$, 2 H), 3.26 (s, O–CH_2, 24 H), 7.15–7.45 (m, Ph, 3 H), 8.67 (m, Ph, 2 H). ^{13}C NMR (C_6D_6): δ 39.9 (s, $=CH_2$), 70.7 (s, O–CH_2), 126–129 (m, Ph), 161.7 (s, Ph). **4**: The same procedure as for **3** was used for **4** using **2** instead of **1** (87%). Anal. Calcd for $C_{20}H_{33}KO_7S$: C, 52.61; H, 7.28. Found: C, 52.80; H, 7.84. ^1H NMR (C_6D_6): δ 2.19 (s, CH_3, 2 H), 2.57 (s, $=CH_2$, 2 H), 3.25 (s, O–CH_2, 24 H), 7.18 (d, Ph, 2 H), 8.63 (d, Ph, 2 H). $[\alpha]_D = +21.7 \pm 3.2°$ (c = 0.930) in THF. **5**: The same procedure as for **3** was used for **5** using kryptofix-2.2.2 instead of 18-crown-6 (73%). Anal. Calcd for $C_{25}H_{43}KN_2O_7S$: C, 54.12; H, 7.81; N, 5.05. Found: C, 54.11; H, 8.00; N, 5.05. ^1H NMR (C_6D_6): δ 2.32 (t, CH_2–N, 12 H), 2.73 (d, $=CH_2$, 2 H), 3.33 (t, O–CH_2, 12 H), 7.05–7.50 (m, Ph, 3 H), 8.84 (m, Ph, 2 H). **6**: The same procedure as for **3** was used for **6** using **2** instead of **1** and kryptofix-2.2.2 instead of 18-crown-6 (65%). Anal. Calcd for $C_{26}H_{45}KN_2O_7S$: C, 54.90; H, 7.97; N, 4.92. Found: C, 54.94; H, 8.36; N, 4.75. ^1H NMR (C_6D_6): δ two isomers 1.13 (t, CH_3, 2/3 3 H), 1.32 (t, CH_3, 1/3 3 H), 2.34 (t, CH_2–N, 12 H), 2.54 (q, $=CH_2$, 1/3 2 H), 2.68 (q, $=CH_2$, 1/3 2 H), 3.33 (t, O–CH_2, 12 H), 3.40 (s, O–CH_2, 12 H), 7.00 (d, Ph, 1/3 2 H), 7.22 (d, Ph, 2/3 2 H), 8.05 (d, Ph, 1/3 2 H), 8.30 (d, Ph, 2/3 2 H). $[\alpha]_D^{20} = 0°$ (c = 0.930) in THF.

(4) Structure of **3**: $C_{19}H_{31}KO_7S$, M = 442.6, monoclinic, space group $P2_1$, a = 9.025 (1) Å, b = 15.799 (2) Å, c = 8.579 (1) Å, β = 107.76 (1)°, U = 1165.0 (3) Å^3, Z = 2, D_c = 1.262 g cm^{-3}, Mo Kα radiation (λ = 0.710 69 Å), μ(Mo Kα) = 3.43 cm^{-1}, crystal dimensions 0.18 × 0.20 × 0.40 mm. The structure was solved by the heavy-atom method (Patterson and Fourier synthesis) and refined anisotropically for all the non-H atoms except S1′ and C27′. The $SOCH_2$ group was found to be disordered about two positions (S, C27 and S′, C27′) sharing the oxygen atom and related by a pseudo-mirror plane running through the Ph ring. The refinement of the positional and thermal parameters converged with site occupation factors of 0.83 and 0.17 for S1, C27 and S1′, C27′ respectively. For 1067 unique observed structure amplitudes [$I > 2\sigma(I)$, no correction for absorption] collected at room temperature on a Siemens AED diffractometer in the range $6 < 2\theta < 46°$, the R value is 0.040 (R_W = 0.041, R_G = 0.048) (R = 0.041, R_W = 0.042, and R_G = 0.050 for the "inverted" structure). The hydrogen atoms, located from a ΔF map, were introduced as fixed contributors (U_{iso} = 0.11 Å^2). During the refinement the Ph rings were constrained to be regular hexagons (C–C = 1.395 Å).

(5) (a) Marsch, M.; Massa, W.; Harms, K.; Baum, G.; Boche, G. *Angew. Chem., Int. Ed. Engl.* **1986,** *25,* 1011. (b) A related lithium α-sulfonyl carbanion has been structurally characterized recently: Gais, H. J.; Muller, J.; Vollhardt, J.; Lindner, H. J. *J. Am. Chem. Soc.* **1991,** *113,* 4002.

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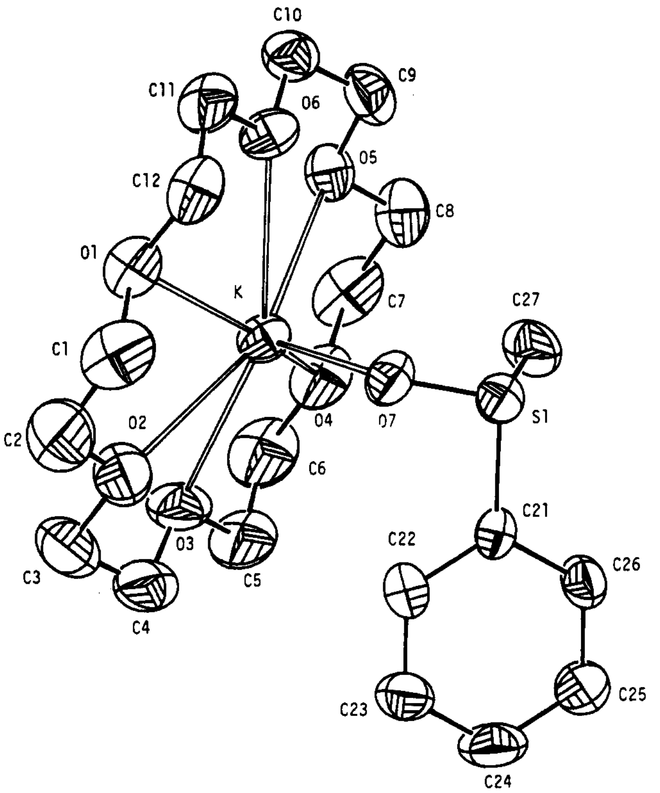


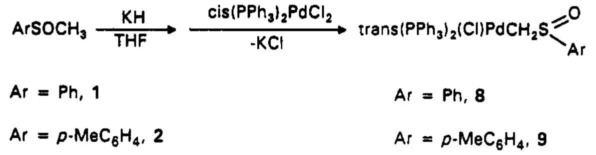
Figure 1. ORTEP view of complex **3** (30% probability ellipsoids). Selected bond distances (Å) and angles (deg) include the following K–O1 = 2.895 (6), K–O2 = 2.832 (7), K–O3 = 2.841 (8), K–O4 = 2.904 (10), K–O5 = 2.986 (6), K–O6 = 2.770 (7), K–O7 = 2.664 (7), S1–O7 = 1.521 (7), S1–C21 = 1.811 (8), S1–C27 = 1.664 (16); C27–S1–C21 = 97.9 (6), O7–S1–C21 = 102.1 (4), O7–S1–C27 = 114.9 (6).

metal-bonded form of the α-sulfenyl anion. Our attention was focused on metals able to bind at the carbon and to assist, eventually, the chemistry of the α-sulfenyl anion. The first attempt was the reaction with $[Cr(CO)_5(THF)]$, which we used recently for binding a variety of enolates in the form of alkylcarbonylmetalates.[6]

$$\underset{4}{ArS(CH_2)O\cdots KL_1} + Cr(CO)_5(THF) \xrightarrow{-THF} \underset{7}{[ArS(O)CH_2Cr(CO)_5\cdots KL_1]} \quad (2)$$

Although we started with the optically pure form of **2**, the sequence of the reaction leading to **7**[7] gave the racemic form of the sulfoxide moiety. We have not yet explored the chemistry of this C-bonded α-sulfenyl anion. A rather similar and unique example, $[(\eta^5\text{-}R_5C_5)(CO)_3WCH_2SOPh]$ (R = H, Me), of a C–metal-bonded α-sulfenyl anion has been reported;[8] however, in this case the sulfoxide is generated via the oxidation of the corresponding sulfide derivative.

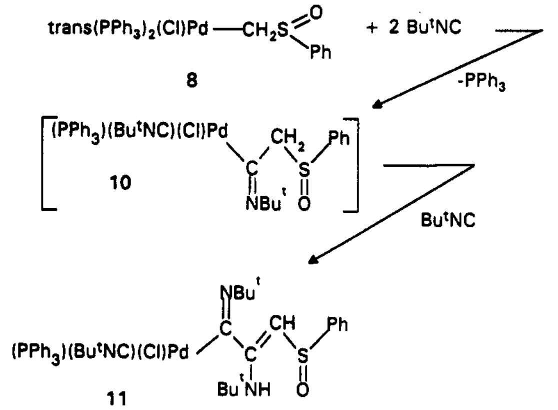
A second approach was to use a metal such as Pd(II), which is used as a transfer agent for a large number of organic functionalities. Reactions of α-sulfenyl anions with olefins in the presence of Pd(II) have been reported, though none of the metallic species involved in the reaction have been identified.[9] Complexation of α-sulfenyl anions was achieved using *cis*-$(PPh_3)_2PdCl_2$.



(3)

Complexes **8**[10] and **9**[10] are stable compounds and can be handled in air. Their characterization includes an X-ray analysis confirming the racemization of the α-sulfenyl moiety in complex **9** and the isomerization of the *cis*- to the *trans*-$(PPh_3)_2Pd$ fragment.

The ionization of the Pd–Cl bond in **8** and **9** is possible by reaction with CF_3SO_3Ag in CH_2Cl_2, freeing up a coordination site on Pd. Palladium can assist in the transfer of the α-sulfenyl anion to substrates which would be unlikely to react with the metal-free form. An example is the migratory insertion of Bu^{t}NC, shown in reaction 4.[11]



(4)

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(6) Veya, P.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Organometallics* **1991**, *10*, 1652, 2991; *J. Chem. Soc., Chem. Commun.* **1991**, 991, 1166.

(7) Procedure for **7** is as follows: A $[Cr(CO)_5(THF)]$ solution, prepared in situ by irradiation of $Cr(CO)_6$ (0.77 g, 3.5 mmol) in THF (250 mL), was added dropwise at –78 °C to a THF (50 mL) solution of **4** (1.57 g, 3.4 mmol). An orange solution was obtained, which was stirred for 5 h and then evaporated to dryness. The oily residue was redissolved in ether (50 mL), yielding a yellow crystalline solid (83%). Anal. Calcd for $C_{25}H_{33}CrKO_{12}S$: C, 46.29; H, 5.13. Found: C, 46.44; H, 5.39. ^{1}H NMR (CD_2Cl_2): δ 1.75–1.96 (2q, CH_2–Cr, 2 H, J = 9.75 Hz), 2.36 (s, CH_3, 3 H), 3.60 (s, O–CH_2, 24 H), 7.22 (d, Ph, 2 H), 7.67 (d, Ph, 2 H). $[\alpha]_D$ = –14.7 ± 1.7° (c = 1.575) in THF. IR (THF solution): ν_{C-O} 2036 (m), 1955 (m), 1899 (s), 1853 (s) cm^{-1}.

(8) (a) Kneuper, H. J.; Zimmermann, C.; Harms, K.; Boche, G. *Chem. Ber.* **1989**, *122*, 1043. (b) A related metal α-sulfonyl complex $[(PPh_3)AuCH(Ph)SO_2Bu^t]$ has also been reported: Kneuper, H. J.; Harms, K.; Boche, G. *J. Organomet. Chem.* **1989**, *364*, 275.

(9) Solladié-Cavallo, A.; Haesslein, J. L. *Helv. Chim. Acta* **1983**, *66*, 1760.

(10) Procedures for **8** and **9** are as follows. **8**: Melted **1** (2.52 g, 18.0 mmol) was added with a syringe to a THF (100 mL) suspension of KH (0.76 g, 18.9 mmol) and the solution stirred overnight. cis-$(PPh_3)_2PdCl_2$ (11.37 g, 16.2 mmol) was added to room temperature resulting in a suspension which was vigorously stirred for 1 day. A white microcrystalline solid formed, which was filtered out, washed with THF (3 × 50 mL), and extracted under inert atmosphere with methylene chloride (50 mL) to eliminate KCl. A white crystalline solid was obtained (90%). Anal. Calcd for $C_{43}H_{37}ClOP_2PdS$: C, 64.11; H, 4.63. Found: C, 64.10; H, 4.68. ^{1}H NMR (CD_2Cl_2): δ 2.15 and 2.20 (t, CH_2–Pd, 1 H), 2.56 (q, CH_2–Pd, 1 H), 6.70 (m, Ph, 2 H), 7.15 (m, Ph, 3 H), 7.48 (m, Ph, 18 H), 7.78 (m, Ph, 12 H). ^{31}P NMR (CD_2Cl_2): δ 29.2 (s). **9**: The same procedure as for **8** was used for **9**, using **2** instead of **1** (90%). Anal. Calcd for $C_{44}H_{39}ClOP_2PdS$: C, 64.48; H, 4.80. Found: C, 63.81; H, 4.93. ^{1}H NMR (CD_2Cl_2): δ 2.20 (2t, CH_2–Pd, 1 H), 2.25 (s, CH_3, 3 H), 2.55 (q, CH_2–Pd, 1 H), 6.65 (d, Ph, 2 H), 6.97 (d, Ph, 2 H), 7.48 (m, PPh, 20 H); 7.79 (m, PPh, 10 H). ^{31}P NMR (CD_2Cl_2): δ 29.0 (s).

(11) Iminoacyl forming from migratory insertion of RNC with M–C bonds is a well-known reaction: Singleton, E.; Oosthnizen, H. E. *Adv. Organomet. Chem.* **1983**, *22*, 209. Otsuka, S.; Nakamura, A.; Yoshida, T.; Naruto, M.; Ataba, K. *J. Am. Chem. Soc.* **1973**, *95*, 3180. Yamamoto, Y.; Yamazaki, H. *Inorg. Chem.* **1974**, *13*, 438. Aoki, K.; Yamamoto, Y. *Inorg. Chem.* **1976**, *15*, 48. Bellachioma, G.; Cardaci, G.; Zanazzi, P. *Inorg. Chem.* **1987**, *26*, 84. Maitlis, P. M.; Espinet, P.; Russell, M. J. H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: London, 1982; Vol. 8, Chapter 38.4. Crociani, B. In *Reactions of Coordinated Ligands*; Braterman, P. S., Ed.; Plenum: New York, 1986; Chapter 9.

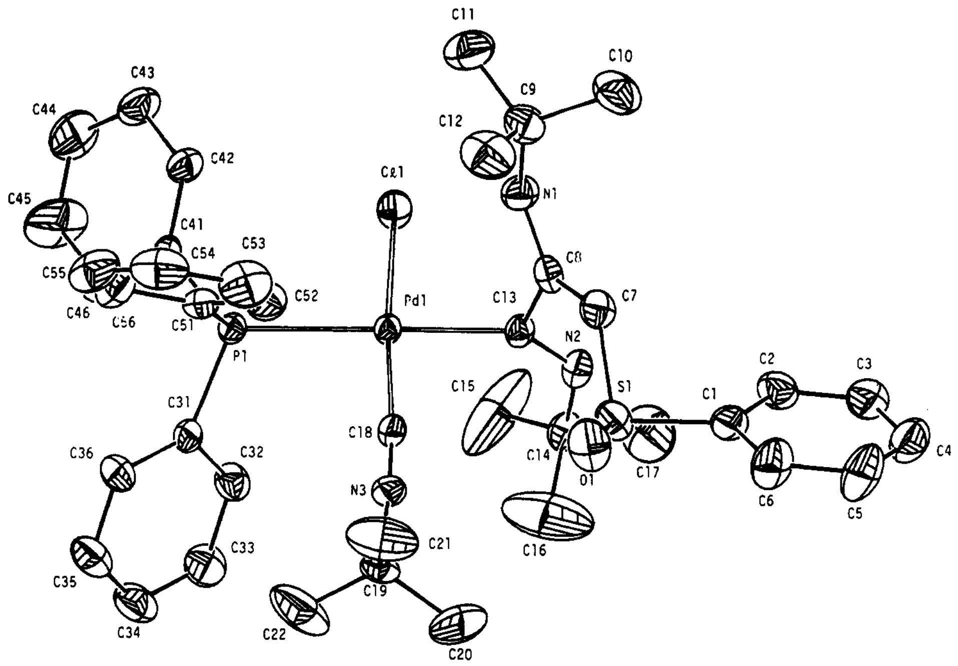

Figure 2. ORTEP view of complex 11 (30% probability ellipsoids). Selected bond distances (Å) and angles (deg) include the following: Pd1–Cl1 = 2.342 (2), Pd1–P1 = 2.408 (1), Pd1–C13 = 2.046 (4), Pd1–C18 = 1.936 (5), N1–C8 = 1.337 (6), C7–C8 = 1.356 (6), C8–C13 = 1.512 (6), N2–C13 = 1.256 (6), S1–C7 = 1.738 (5), S1–O1 = 1.496 (5), S1–C1 = 1.779 (3); C13–Pd1–C18 = 85.9 (2), P1–Pd1–C18 = 89.1 (1), P1–Pd1–C13 = 172.0 (1), Cl1–Pd1–C18 = 174.9 (1), Cl1–Pd1–C13 = 89.4 (1), S1–C7–C8 = 122.5 (4), C1–S1–C7 = 99.6 (2), O1–S1–C7 = 107.0 (2), O1–S1–C1 = 105.2 (2).

In reaction 4, one of the triphenylphosphines was replaced by an isocyanide ligand and the double insertion of Bu^{t}NC was followed by the enolization of one of the imino groups in complex 11 (ca. 80%).[12] Its structure[13] is shown in Figure 2. For the organic fragment derived from the insertion reaction, the bonding scheme and geometry are supported by the structural parameters given in the caption to Figure 2. The two Pd–C bond distances suggest a pure σ bond for Pd–C13[14] and some multiple bond character for Pd–C18.[15] The N1–C8–C7–S1 moiety is almost planar with a torsion angle of −167.2 (4)°. The enolization of the methylene group is proved by the C7–C8 bond distance [1.356 (6) Å]. Other metal-assisted reactions of α-sulfenyl anions are under investigation.

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Supplementary Material Available: For 3 and 11, tables of crystal data, atomic coordinates, anisotropic thermal parameters, and bond distances and angles (Tables 1–9) (11 pages). Ordering information is given on any current masthead page.

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[12] Procedure for 11 is as follows. To a THF (40 mL) suspension of 8 (2.13 g, 2.64 mmol) was added dropwise a THF (20 mL) solution of Bu^{t}NC (0.90 g, 10.8 mmol). A limpid solution was suddenly obtained, solvent was evaporated, and the crude oily product was redissolved in ether (50 mL). White crystals formed slowly (81%). Anal. Calcd for $C_{40}H_{49}ClN_3OPPdS$: C, 60.60; H, 6.23; N, 5.30. Found: C, 60.39; H, 6.39; N, 5.07. ^1H NMR (C_6D_6): δ 1.05 (s, Bu^t, 9 H), 1.17 (s, Bu^t, 9 H), 1.88 (s, Bu^t, 9 H), 5.11 (d, =CH–SO, 1 H), 6.90–7.10 (m, Ph, 12 H), 7.7 (m, Ph, 6 H), 8.55 (m, Ph, 2 H). ^{31}P NMR (C_6D_6): δ 12.3 (s). IR (nujol): ν_{N-H} 3309 (w), ν_{N-C} 2206 (s), ν_{C-N} 1632 (s) cm^{-1}.

[13] Structure of 11: $C_{40}H_{49}ClN_3OPPdS$, $M = 792.7$, monoclinic, space group $C2/c$, $a = 43.577$ (4) Å, $b = 9.214$ (1) Å, $c = 20.752$ (2) Å, $\beta = 101.20$ (1)°, $U = 8173.6$ (14) Å^3, $Z = 8$, $D_c = 1.288$ g cm^{-3}, Mo Kα radiation (λ = 0.710 69 Å), μ(Mo Kα) = 6.32 cm^{-1}; crystal dimensions 0.32 × 0.45 × 0.62 mm. The structure was solved by the heavy-atom method (Patterson and Fourier synthesis) and refined anisotropically for all the non-H atoms. For 4417 unique observed structure amplitudes $[I > 2\sigma(I)]$ collected at room temperature on a Philips PW 1100 diffractometer in the range $6 < 2\theta < 50°$ not corrected for absorption, the R value is 0.037 ($R_W = 0.041$). The hydrogen atoms, located from a ΔF map, were introduced as fixed contributors ($U_{iso} = 0.08$ Å^2). During the refinement the Ph rings were constrained to be regular hexagons (C–C = 1.395 Å).

[14] Crociani, B.; Bandoli, G.; Clemente, D. A. *J. Organomet. Chem.* 1980, *184*, 269.

[15] Kitano, Y.; Hori, T. *Acta Crystallogr., Sect. B* 1981, *B37*, 1919.