propane. Bands corresponding to the trans isomer at 2271, 1024, 1041, and 849 cm^{-1} were absent.[19] This result demonstrates that cyclopropane formation occurs with inversion of stereochemistry at the carbon bound to iron. This result supports a mechanism involving backside attack of the electrophilic γ-carbon at the iron–carbon bond through a W-shaped intermediate and is inconsistent with a mechanism involving a metallacyclobutane intermediate.

Earlier we had attempted to explain the formation of cis cyclopropanes from $(CO)_5W{=}CHPh$ and *cis*-$CH_3HC{=}CHCH_3$ or $(CH_3)_2C{=}CHCH_3$ by a mechanism involving interaction of the ipso carbon of the aryl ring on C_α with the more substituted alkene carbon followed by conversion to a metallacycle and reductive elimination.[20] The results here demonstrating inversion of stereochemistry at the α-carbon strongly suggest that this explanation is incorrect. Since this constitutes our second retraction of explanations for the stereochemistry of the product cyclopropanes, we are reluctant to offer a third at this time.

Acknowledgment. We wish to thank Maurice Brookhart for informing us of his related work prior to publication and Jerome Berson for providing IR spectra of *cis*- and *trans*-dideuteriocyclopropane. Financial support from the National Science Foundation is gratefully acknowledged.

Registry No. 1-CF_3SO_3, 122171-43-1; 1-d_2, 122171-48-6; **2**, 122171-44-2; **2**-d_2, 122171-46-4; **3**, 71350-90-8; **3**-d_2, 122171-41-9; **4**, 13482-13-8; **5**, 122171-40-8; $Na^+[C_5H_5(CO)_2Fe]^-$, 122171-45-3; (*R**,*S**)-BrCHDCHDOH, 80236-19-7; cyclopropane, 75-19-4; acetylene-d_2, 1070-74-2; *trans*-1,2-dideuterioethylene, 1517-53-9; ((phenylthio)methyl)lithium, 13307-75-0; *cis*-1,2-dideuteriocyclopropane, 122211-66-9.

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[19] (a) Pedersen, L. D. Ph.D. Dissertation, Yale University, 1975. (b) Berson, J. A.; Pedersen, L. D.; Carpenter, B. K. *J. Am. Chem. Soc.* **1976**, *98*, 122.

[20] Casey, C. P.; Polichnowski, S. W.; Shusterman, A. J.; Jones, C. R. *J. Am. Chem. Soc.* **1979**, *101*, 7282.

Reactions of Chloro((tri-2,4,6-*tert*-butylphenyl)imino)phosphane with Anionic Transition-Metal Complexes: Stable Metalloiminophosphanes and Evidence for Terminal Aminophosphinidene Complexes

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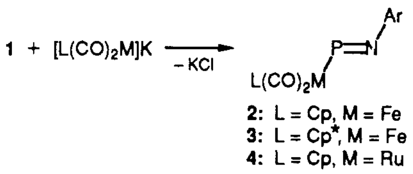
Summary: Reaction of $[(Cl)P{=}N(2,4,6\text{-}(t\text{-}Bu)_3C_6H_2)]$ (**1**) with $[(\eta^5\text{-}Me_5C_5)(CO)_2Fe]K$ affords the stable metalloiminophosphane $[(\eta^5\text{-}Me_5C_5)(CO)_2FeP{=}N(2,4,6\text{-}(t\text{-}Bu)_3C_6H_2)]$ (**3**), the structure of which was determined by X-ray crystallography. Rearrangement of the tungsten compound $[(\eta^5\text{-}Me_5C_5)_2W(H)(PN(2,4,6\text{-}(t\text{-}Bu)_3C_6H_2)]$ (**6**) via a 1,3-hydrogen shift results in the formation of the terminal aminophosphinidene complex $[(\eta^5\text{-}Me_5C_5)_2WPN(H)(2,4,6\text{-}(t\text{-}Bu)_3C_6H_2)]$ (**7**), identified spectroscopically.

A variety of iminophosphane complexes is known,[1] demonstrating the versatility of phosphorus–element pπ systems as ligands. So far only η^1-coordination to one metal fragment has been observed with the iminophosphane acting as a two-electron donor via the lone pair at the phosphorus atom. However, organometal-substituted iminophosphanes of the type $L_nMP{=}NR$, i.e. the P=N moiety acting as one-electron donor, have so far only been postulated as intermediates[2] or could only be detected spectroscopically due to decomposition at room temperature as for $L_nM = (R_3P)(CO)Ni$.[3] Here, we report on the first stable metalloiminophosphanes, $L(CO)_2MP{=}NAr$ (L = Cp (η^5-C_5H_5), M = Fe, Ru; L = Cp* (η^5-C_5Me_5), M = Fe; Ar = 2,4,6-*t*-$Bu_3C_6H_2$), the synthesis of which had been prompted by the recent discovery of the chloroiminophosphane **1**.[4] This concept is analogous to the preparation of $[Cp^*(CO)_2FeP{=}C(SiMe_3)_2]$[5] from $[ClP{=}C(SiMe_3)_2]$, and thus, after phosphavinyl complexes and metallodiphosphenes,[6] organometal-substituted iminophosphanes have become accessible.

Scheme I



In a typical preparation a pentane solution of **1** (1.63 g, 5 mmol) was added to a solution of an equimolar quantity of $[Cp^*(CO)_2Fe]K$ in tetrahydrofuran at 0 °C. After being warmed to room temperature, the dark brown reaction mixture was stirred for 15 h and filtered and the filtrate evaporated to dryness. Recrystallization from petroleum ether (bp 40–60 °C) at −30 °C afforded dark brown **3**.[7] [Attempts to prepare P-metalated iminophosphanes from anionic group VIB transition-metal complexes $[L(CO)_3M]M'$ (L = Cp, Cp*; M = Cr, Mo, W; M′ = Li, Na, K) failed so far due to the thermal instability of the resulting products. Only ^{31}P NMR spectroscopic evidence could be obtained for a tungsten compound assumed to be $[Cp^*(CO)_3WP{=}NAr]$ (δ = 754 ppm), which decomposes rapidly at temperatures above −40 °C.] The reactions with $[Cp(CO)_2Fe]K$ and $[Cp(CO)_2Ru]K$ were performed analogously and furnished products **2** and **4**, respectively. In the $^{31}P\{^1H\}$NMR spectra the signals for **2**, **3**, and **4** are found, as expected, at extremely low field, viz. δ = 717, 787, and 688 ppm (H_3PO_4 external, C_6D_6), respectively. These low-field shifts are accounted for by the organo-

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[1] (a) Scherer, O. J.; Konrad, R.; Guggolz, E.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 297. (b) Scherer, O. J.; Kerth, J. Asselmann, R. Sheldrick, W. S. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 984. (c) Arif, A. M.; Cowley, A. H.; Pakulski, M. *J. Am. Chem. Soc.* **1985**, *107*, 2553.

[2] Gudat, D.; Niecke, E.; Krebs, B.; Dartmann, M. *Organometallics* **1986**, *5*, 2376.

[3] Gudat, D.; Niecke, E. *J. Chem. Soc., Chem. Commun.* **1987**, 10.

[4] Niecke, E.; Nieger, M.; Reichert, F. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1715.

[5] Gudat, D.; Niecke, E.; Arif, A. M.; Cowley, A. H.; Quashie, S. *Organometallics* **1986**, *5*, 593.

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

[7] Data for compounds **2**, **3**, and **4**: MS (EI, 70 eV, *m/e* (relative intensity)); ^1H NMR (δ, C_6D_6); $^{13}C\{^1H\}$ (δ, C_6D_6); $^{31}P\{^1H\}$ (δ, C_6D_6); IR (cm^{-1}, pentane). **2**: IR 2037 s, 1983 s; MS 467 (<1, M^+), 346 (2, $M^+ - 2CO - Cp$); ^1H 1.4 (s, 18 H, *o*-tBu), 1.5 (s, 9 H, *p*-tBu), 4.4 (s, 5 H, C_5H_5), 7.6 (s (br), 2 H, C_6H_2); $^{13}C\{^1H\}$ 211.5 ($Fe(CO)_2$), 87.6 (d, *J* = 5 Hz, C_5H_5); $^{31}P\{^1H\}$ 717. **3**: IR 1998 s, 1953 s; MS 537 (M^+, 10), 481 (83, $M^+ - 2CO$); ^1H 1.1 (d(br), *J* = 3 Hz, 15 H, C_5Me_5), 1.2 (s, 9 H, *p*-tBu), 1.3 (s, 18 H, *o*-tBu), 7.3 (s (br), 2 H, $tBu_3C_6H_2$); $^{13}C\{^1H\}$ 213.6 ($Fe(CO)_2$), 154.8 (PNCCC*C*), 141.0 (PNC*C*), 129.9 (d, *J* = 30 Hz, PNC), 121.5 (PNCC*C*), 98.7 (*C*$_5$Me$_5$); 36.2, 34.7, 32.2 (CMe_3), 9.1 (d, *J* = 7 Hz, C$_5$*Me*$_5$). $^{31}P\{^1H\}$ 787. **4**: IR 2022 s, 1982 s; MS 513 (<1, M^+), 457 (<1, $M^+ - 2CO$); ^1H 1.5 (s, 18 H, *o*-tBu), 1.5 (s, 9 H, *p*-tBu), 4.7 (s, 5 H, C_5H_5), 7.6 (s, 2 H, C_6H_2); $^{13}C\{^1H\}$ 201.7 ($Ru(CO)_2$), 90.5 (d, *J* = 3 Hz, C_5H_5); $^{31}P\{^1H\}$ 688. The ^{13}C NMR data for the 2,4,6-*t*-$Bu_3C_6H_2$ groups of compounds **2** and **4** are very similar to those observed for **3**.

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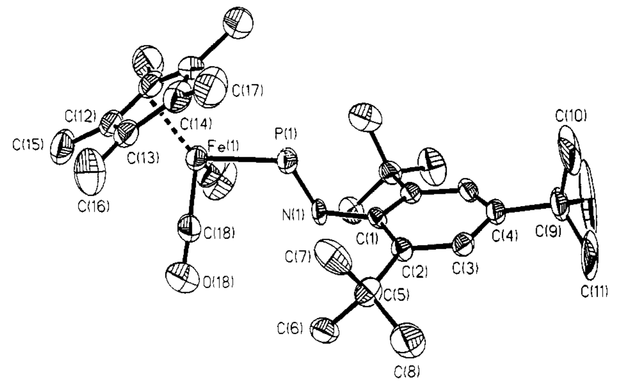


Figure 1. Structure of [Cp*(CO)$_2$FeP=NAr] (**3**) showing the atom numbering scheme. Important bond lengths (pm) and angles (deg): P1–Fe1, 220.5 (5); P1–N1, 156.4 (12); N1–C1, 140.8 (7); Fe1–P1–N1, 115.4 (5); P1–N1–C1, 119.8 (9). The atoms C12, C15, Fe1, P1, N1, C1, C4, C9, and C10 are lying in a mirror plane.

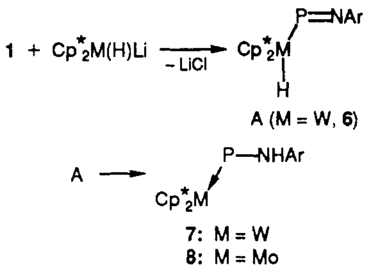
metallic substituents in that they inductively destabilize the HOMO (n_p), thus increasing the paramagnetic shift contribution. Moreover, this exemplifies once more the increased σ-donor strength going from Cp- to Cp*-ligated metal fragments.

An X-ray structure analysis of **3**[8] revealed some informative features: In contrast to the cis configuration in **1**, the metalloiminophosphane displays a trans configuration in the solid state. The reduction of s character of the PN bond is demonstrated by the lengthening of this bond to 156 pm (cf. 149 pm for **1**), which corresponds to a double bond, and establishes an essentially sp^2-hybridized P atom. This is further corroborated by the Fe–P–N and the P–N–C1 angles, 115° and 120°, respectively. The relatively large valence angle at phosphorus, the largest found in *trans*-iminophosphanes,[9] has to be attributed to the iron fragment being a very effective σ-donor since steric reasons cannot be put forward. In any case replacing a σ-acceptor (Cl) by a σ-donor effects a drastic change of the electronic constitution.

As in [Cp*(CO)$_2$FeP=PAr][6] the iminophosphane ligand in **3** can also be viewed as one leg of a distorted three-legged piano-stool arrangement. The FeP bond length of 220 ppm, though lying in the range of single bond distances,[10] appears somewhat shortened in comparison to 226.0 pm found in the above diphosphenyl complex. This implies a weak intramolecular donor/acceptor interacraction of filled metal d orbitals with the $\pi^*_{\mathrm{P=N}}$-orbital.

In a heterogeneous reaction, **1** has also been treated with the lithiated bis(pentamethylcyclopentadienyl) dihydrido species of molybdenum and tungsten[11] at ambient temperatures. Examination of the ^{31}P{^{1}H} NMR spectra of the reaction mixtures strongly suggests the formation of the terminal aminophosphinidene complexes **7** and **8**. Support for this proposal is gained from comparison of their spectroscopic data[12] with those of the compounds having been obtained by Lappert et al.[13] Thus the chemical shift values of 770 and 663 ppm for **7** and **8**, respectively, and in the case of tungsten the coupling to phosphorus (^1J(^{183}W^{31}P) = 147 Hz) are clearly indicative of the above-mentioned class of complexes. Moreover, theoretical investigations[14] have shown that for phosphinidenes bearing stabilizing π-donors in the α-position (e.g. H_2N—P being of course isomeric to HN=PH) a planar singlet ground state is favored. An aminophosphinidene moiety thus should combine quite favorably with an electron-deficient "Cp*$_2$W metallocene" fragment with its "bent-off" cyclopentadienyl rings (cf. Cp*$_2$WH$_2$).

Scheme II



The formation of **7** and **8** might involve the intermediacy of hydridometalloiminophosphanes, which would then undergo 1,3-hydrogen shift to rearrange to the final products. Such a possible intermediate, **6**, has been shown to exist for M = W by a low-temperature NMR experiment. The signal of **6** (754 ppm) slowly decreases while the signal of **7** increases on warming a sample very slowly from −40 °C to room temperature. Rearrangements of this type involving groups of high migratory aptitude such as H or Me$_3$Si are not uncommon in this field of chemistry, e.g. for certain diphosphatriazenes and alkyliminophosphanes to produce the corresponding aminodiphosphenes and aminophosphaalkenes, respectively.[15]

The above-mentioned compounds, however, have so far defied all attempts of purification or isolation, thus rendering impossible unequivocal characterization, especially by means of X-ray diffraction.

Further efforts to achieve full characterization are therefore currently in progress, as are further studies concerning the reactivity of **1** toward transition-metal complexes.

Acknowledgment. We are grateful to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for a scholarship (to J.H.).

Registry No. **1**, 117688-09-2; **2**, 122172-05-8; **3**, 122172-06-9; **4**, 122172-07-0; **6**, 122188-49-2; **7**, 122172-08-1; **8**, 122172-09-2; [Cp*(CO)$_2$Fe]K, 59654-59-0; [Cp(CO)$_2$Fe]K, 60039-75-0; [Cp(CO)$_2$Ru]K, 84332-45-6; [Cp*(CO)$_3$WP=NAr], 122188-66-3; Cp$_2$*Mo(H)Li, 122172-10-5; Cp$_2$*W(H)Li, 122172-11-6.

Supplementary Material Available: Tables of final atomic coordinates, isotropic thermal parameters, and bond lengths and angles (5 pages); a listing final observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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[8] Some crystal data for **3** are as follows: $C_{30}H_{44}FeNO_2P$, M = 537.5, tetragonal, space group *P*4/*mcc* (No. 124); a = 1980.0 (7) pm, c = 1785.5 (7) pm, V = 7.001 nm^3, Z = 8, d_{calcd} = 1.04 g cm^{-3}, μ (Mo Kα) = 0.50 mm^{-1}. A total of 2393 symmetry-independent reflections were recorded with $2\theta_{\mathrm{max}} = 45°$. Of these, 1259 reflections ($|F| > 4\sigma(P)$) were used to solve (direct methods) and refine (174 parameters) the structure of **3**. Nonhydrogen atoms were refined aniosotropically. R = 0.116 (R_w = 0.100; $w = \sigma^2(P) + 0.001F^2$). The nonsatisfactory R value is due to decomposition of the crystal during measurement. No suitable single crystals were available for a low-temperature X-ray structure determination. Solvent was not identified.

[9] Markovskii, L. N.; Romanenko, V. D.; Ruban, A. V. *Chemie acyclischer doppeltkoordinierter Phosphorverbindungen*: Kiew, 1988 and references cited therein.

[10] Corbridge, D. E. C. *The Structural Chemistry of Phosphorus*; Elsevier: Amsterdam, 1974.

[11] Francis, B. R.; Green, M. L. H.; Luong-thi, T.; Moser, G. A. *J. Chem. Soc., Dalton Trans.* **1976**, 1339.

[12] **7**: ^{13}C{^{1}H} δ 76.0 (C_5H_5); ^{31}P{^{1}H} δ 770; ^{31}P δ 770 (d, J = 7 Hz). **8**: ^{13}C{^{1}H} δ 71.6 (C_5H_5, J(WC) = 5 Hz); ^{31}P{^{1}H} δ 663 (J(WP) = 147 Hz); ^{31}P δ 663 (d, J = 5 Hz).

[13] Hitchcock, P. B.; Lappert, M. F.; Leung, W.-P. *J. Chem. Soc., Chem. Commun.* **1987**, 1282.

[14] Trinquier, G.; Bertrand, G. *Inorg. Chem.* **1985**, *24*, 3842.

[15] Lysek, M. Dissertation, Bielefeld, 1987.