

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 $(\text{CO})_5\text{W}=\text{CHPh}$ and *cis*- $\text{CH}_3\text{HC}=\text{CHCH}_3$ or $(\text{CH}_3)_2\text{C}=\text{CHCH}_3$ 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.

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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; $\text{Na}^+[\text{C}_6\text{H}_5(\text{CO})_2\text{Fe}]^-$, 122171-45-3; (R^*, S^*)-BrCHDCHDOH, 80236-19-7; cyclopropane, 75-19-4; acetylene- d_2 , 1070-74-2; *trans*-1,2-dideuteroethylene, 1517-53-9; ((phenylthio)methyl)lithium, 13307-75-0; *cis*-1,2-dideuteriocyclopropane, 122211-66-9.

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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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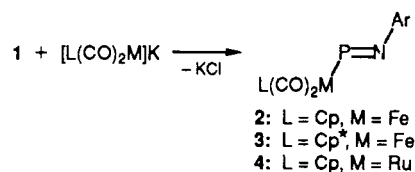
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Summary: Reaction of $[(\text{Cl})\text{P}=\text{N}(2,4,6\text{-}(t\text{-Bu})_3\text{C}_6\text{H}_2)]$ (1) with $[(\eta^5\text{-Me}_5\text{C}_5)(\text{CO})_2\text{Fe}]\text{K}$ affords the stable metalloiminophosphane $[(\eta^5\text{-Me}_5\text{C}_5)(\text{CO})_2\text{FeP}=\text{N}(2,4,6\text{-}(t\text{-Bu})_3\text{C}_6\text{H}_2)]$ (3), the structure of which was determined by X-ray crystallography. Rearrangement of the tungsten compound $[(\eta^5\text{-Me}_5\text{C}_5)_2\text{W}(\text{H})(\text{PN}(2,4,6\text{-}(t\text{-Bu})_3\text{C}_6\text{H}_2))]$ (6) via a 1,3-hydrogen shift results in the formation of the terminal aminophosphinidene complex $[(\eta^5\text{-Me}_5\text{C}_5)_2\text{WPN}(\text{H})(2,4,6\text{-}(t\text{-Bu})_3\text{C}_6\text{H}_2)]$ (7), identified spectroscopically.

A variety of iminophosphane complexes is known,¹ demonstrating the versatility of phosphorus-element π systems as ligands. So far only η^1 -coordination to one metal fragment has been observed with the imino-

Scheme I



phosphane acting as a two-electron donor via the lone pair at the phosphorus atom. However, organometal-substituted iminophosphanes of the type $\text{L}_n\text{MP}=\text{NR}$, i.e. the $\text{P}=\text{N}$ moiety acting as one-electron donor, have so far only been postulated as intermediates² or could only be detected spectroscopically due to decomposition at room temperature as for $\text{L}_n\text{M} = (\text{R}_3\text{P})(\text{CO})\text{Ni}$.³ Here, we report on the first stable metalloiminophosphane, $\text{L}(\text{CO})_2\text{MP}=\text{NAr}$ (L = Cp ($\eta^5\text{-C}_5\text{H}_5$), M = Fe, Ru; L = Cp* ($\eta^5\text{-C}_5\text{Me}_5$), M = Fe; Ar = 2,4,6-*t*-Bu₃C₆H₂), the synthesis of which had been prompted by the recent discovery of the chloroiminophosphane 1.⁴ This concept is analogous to the preparation of $[\text{Cp}^*(\text{CO})_2\text{FeP}=\text{C}(\text{SiMe}_3)_2]$ ⁵ from $[\text{ClP}=\text{C}(\text{SiMe}_3)_2]$, and thus, after phosphavinyl complexes and metallodiphosphenes,⁶ organometal-substituted iminophosphanes have become accessible.

In a typical preparation a pentane solution of 1 (1.63 g, 5 mmol) was added to a solution of an equimolar quantity of $[\text{Cp}^*(\text{CO})_2\text{Fe}]\text{K}$ 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 $[\text{L}(\text{CO})_3\text{M}]\text{M}'$ (L = Cp, Cp*; M = Cr, Mo, W; M' = Li, Na, K) failed so far due to the thermal instability of the resulting products. Only ³¹P NMR spectroscopic evidence could be obtained for a tungsten compound assumed to be $[\text{Cp}^*(\text{CO})_3\text{WP}=\text{NAr}]$ (δ = 754 ppm), which decomposes rapidly at temperatures above –40 °C.] The reactions with $[\text{Cp}(\text{CO})_2\text{Fe}]\text{K}$ and $[\text{Cp}(\text{CO})_2\text{Ru}]\text{K}$ were performed analogously and furnished products 2 and 4, respectively. In the ³¹P{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, C₆D₆), respectively. These low-field shifts are accounted for by the organo-

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(7) Data for compounds 2, 3, and 4: MS (EI, 70 eV, *m/e* (relative intensity)); ¹H NMR (δ , C₆D₆); ¹³C{¹H} (δ , C₆D₆); ³¹P{¹H} (δ , C₆D₆); 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, C₅H₅), 7.6 (s (br), 2 H, C₆H₂); ¹³C{¹H} 211.5 (Fe(CO)₂), 87.6 (d, *J* = 5 Hz, C₅H₅); ³¹P{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, C₅Me₅), 1.2 (s, 9 H, *p*-tBu), 1.3 (s, 18 H, *o*-tBu), 7.3 (s (br), 2 H, tBu₃C₆H₂); ¹³C{¹H} 213.6 (Fe(CO)₂), 154.8 (PNC-CCC), 141.0 (PNCC), 129.9 (d, *J* = 30 Hz, PNC), 121.5 (PNCCC), 98.7 (C₅Me₅), 36.2, 34.7, 32.2 (CMe₃), 9.1 (d, *J* = 7 Hz, C₅Me₅). ³¹P{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, C₅H₅), 7.6 (s, 2 H, C₆H₂); ¹³C{¹H} 201.7 (Ru(CO)₂), 90.5 (d, *J* = 3 Hz, C₅H₅); ³¹P{¹H} 688. The ¹³C NMR data for the 2,4,6-*t*-Bu₃C₆H₂ groups of compounds 2 and 4 are very similar to those observed for 3.

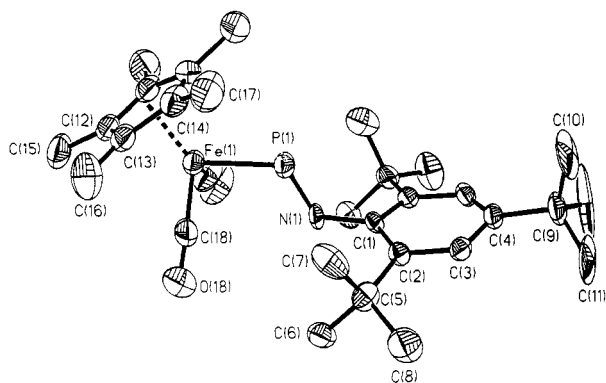


Figure 1. Structure of $[\text{Cp}^*(\text{CO})_2\text{FeP}=\text{NAr}]$ (**3**) showing the atom numbering scheme. Important bond lengths (pm) and angles (deg): P1–Fe1, 220.5 (5); P1–N1, 156.4 (12); N1–C1, 140.8 (7); Fe1–P1–N1, 115.4 (5); P1–N1–C1, 119.8 (9). The atoms C12, C15, Fe1, P1, N1, C1, C4,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

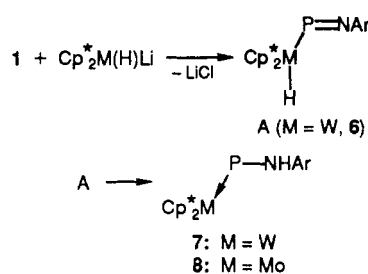
metallic substituents in that they inductively destabilize the HOMO (n_p), thus increasing the paramagnetic shift contribution. Moreover, this exemplifies once more the increased σ -donor strength going from Cp- to Cp*-ligated metal fragments.

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 $[\text{Cp}^*(\text{CO})_2\text{FeP}=\text{PAR}]$ 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 pm, 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 interaction of filled metal d orbitals with the $\pi^*_{\text{P}=\text{N}}$ -orbital.

In a heterogeneous reaction, **1** has also been treated with the lithiated bis(pentamethylcyclopentadienyl) dihydrido species of molybdenum and tungsten¹¹ at ambient temperatures. Examination of the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the reaction mixtures strongly suggests the formation of the terminal aminophosphinidene complexes **7** and **8**. Support

Scheme II



for this proposal is gained from comparison of their spectroscopic data¹² 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 -($^{183}\text{W}^{31}\text{P}$) = 147 Hz) are clearly indicative of the above-mentioned class of complexes. Moreover, theoretical investigations¹⁴ have shown that for phosphinidenes bearing stabilizing π -donors in the α -position (e.g. $\text{H}_2\text{N}-\text{P}$ being of course isomeric to $\text{HN}=\text{PH}$) 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).

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 $\text{M} = \text{W}$ 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_3Si are not uncommon in this field of chemistry, e.g. for certain diphosphatriazenes and alkyliminophosphanes to produce the corresponding aminodiphosphanes 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.

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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; $[\text{Cp}^*(\text{CO})_2\text{Fe}]K$, 59654-59-0; $[\text{Cp}(\text{CO})_2\text{Fe}]K$, 60039-75-0; $[\text{Cp}(\text{CO})_2\text{Ru}]K$, 84332-45-6; $[\text{Cp}^*(\text{CO})_3\text{WP}=\text{NAr}]$, 122188-66-3; $\text{Cp}_2^*\text{Mo}(\text{H})\text{Li}$, 122172-10-5; $\text{Cp}_2^*\text{W}(\text{H})\text{Li}$, 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.

(8) Some crystal data for **3** are as follows: $\text{C}_{30}\text{H}_{44}\text{FeNO}_2\text{P}$, $M = 537.5$, tetragonal, space group $P4/mcc$ (No. 124); $a = 1980.0$ (7) pm, $c = 1785.5$ (7) pm, $V = 7.001 \text{ nm}^3$, $Z = 8$, $d_{\text{calc}} = 1.04 \text{ g cm}^{-3}$, μ (Mo $K\alpha$) = 0.50 mm^{-1} . A total of 2393 symmetry-independent reflections were recorded with $2\theta_{\text{max}} = 45^\circ$. Of these, 1259 reflections ($|F| > 4\sigma(P)$) were used to solve (direct methods) and refine (174 parameters) the structure of **3**. Non-hydrogen atoms were refined anisotropically. $R = 0.116$ ($R_w = 0.100$; $w = \sigma^2(P) + 0.001F^2$). 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.

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

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