

# P-H-functionalized Ylide-Carbene Complexes: Synthesis of $[(\text{CO})_5\text{M}=\text{C}(\text{OEt})\text{CH}=\text{P}(\text{NPr}_i)_2\text{H}]$ ( $\text{M} = \text{Cr}, \text{W}$ ) and Structure of the Chromium Derivative

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$(\text{CO})_5\text{M}=\text{C}(\text{OEt})\text{CH}_2\text{Li}$  **1a,b** ( $\text{M}$ : **a**, Cr; **b**, W) react with  $\text{ClP}(\text{NPr}_i)_2$  **2** to yield the P-H-functionalized ylide-carbene complexes **4a,b** via transiently formed  $[\alpha$ -(phosphino)alkyl]carbene complexes **3a,b**; compounds **4a,b** are characterized by NMR spectroscopy ( $^{13}\text{C}$ ,  $^{31}\text{P}$ ) and complex **4a** by single crystal X-ray diffraction.

Very recently, Fischer-type  $[\alpha$ -(trimethylsilyl)alkyl]carbene complexes were synthesized by Macomber and coworkers.<sup>1</sup> These complexes have been employed to synthesize  $\alpha$ -substituted alkenylaminocarbene transition metal complexes in a modified Peterson reaction.<sup>2</sup> However, the reactivity of isolobal  $[\alpha$ -(trimethylphosphonio)alkyl]carbene transition metal complexes, which have been synthesized by alkylation of ylide-carbene complexes,<sup>3</sup> has not been investigated.

Surprisingly, the  $[\alpha$ -(phosphino)alkyl]carbene complexes are still unknown, but they might be expected to have interesting reaction properties.

Here we report our synthetic approach to  $\alpha$ -phosphino-substituted (ethoxycarbene)-chromium(0) and -tungsten(0) complexes. *In situ* generated lithio compounds **1a,b** react with the bis(diisopropylamino)chlorophosphane **2** at  $-78^\circ\text{C}$  to give compounds **3a,b** ( $\text{M}$ : **a**, Cr; **b**, W throughout) as reactive intermediates. The  $\alpha$ -phosphino-substituted derivatives **3a,b** are unexpectedly unstable in solution at ambient temperature;† rearrangement of **3a,b**, monitored by  $^{31}\text{P}$  NMR spectroscopy (**3a**:  $\delta$  51.36; **3b**:  $\delta$  53.61), led to the formation of the

ylide-carbene complexes **4a,b**‡ probably via a 1,2-hydrogen shift (Scheme 1). In contrast to established routes to ylide-carbene complexes, which are commonly generated by reaction of metal carbonyls and phosphorus ylide derivatives,<sup>5,6</sup> the compounds **4a,b** represent the first P-H-functionalized ylide-carbene complexes obtained by rearrangement reactions.

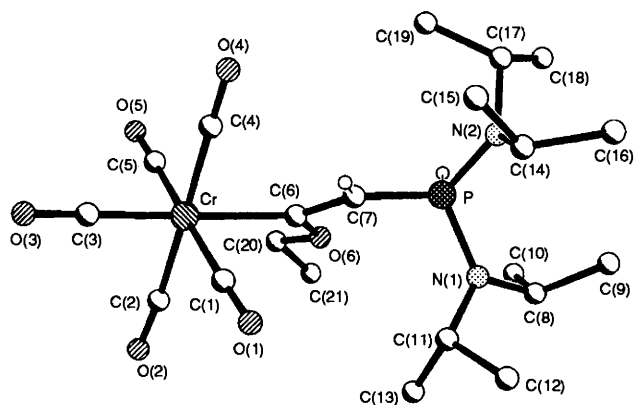
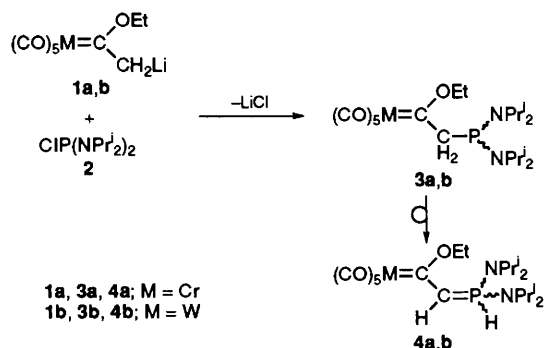
The composition and structure of **4a,b** are confirmed by elemental analysis, mass spectrometric and IR and NMR spectroscopic investigations.§ The existence of a P-H bond in **4a,b** is clearly established by the very large  $^1J_{\text{PH}}$  coupling constant of 535.0 **4a** and 535.3 Hz **4b**. The  $^{13}\text{C}$  NMR resonance of the carbene atoms of **4a,b** is significantly upfield-shifted in comparison to their educts.

The X-ray crystal structure analysis of **4a** (Fig. 1)¶ shows an *s-trans*-configured Cr-C-P skeleton with Cr-C(6) [214.7(5) pm] and C(7)-P [173.2(5) pm] bond lengths that indicate significantly lengthened Cr=C and P=C double bonds. The short C(6)-C(7) bond [138.0(7) pm] implies some contribution from a phosphoniovinyl resonance form to complex **4a**.

The increased  $\pi$ -bonding stabilization of the carbene atoms of **4a,b** associated with this ylide substituent, implies that the carbene ligand becomes a weaker  $\pi$ -acceptor towards the chromium. This results in increased back bonding to the carbonyl ligands, particularly to the *trans*-CO ligand [Cr-C(3) 184.6(6) pm]. The Cr-C(5) distance is 188.2(6) pm (*cis*-CO) which stresses the strong *trans* effect.

We are currently investigating the reactivity of **4a,b**. This work was supported by a grant to R. S. from the Fonds der Chemischen Industrie and by the BASF AG.

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**Fig. 1** Molecular structure of complex **4a** in the crystal. Radii are arbitrary. Only the chemically important H atoms at P and C(7) (identified unambiguously in difference maps) are shown. Selected bond lengths (pm) and angles ( $^\circ$ ): Cr-C(6), 214.7(5); C(6)-C(7), 138.0(7); C(7)-P, 173.2(5); Cr-C(3), 184.6(6); Cr-C(5), 188.2(6); C(7)-C(6)-Cr, 121.1(4); O(6)-C(6)-Cr, 128.7(3); torsion angle Cr-C(6)-C(7)-P, 0.4.

## Footnotes

† Because of the instability of **3a,b**, no further characterising data could be obtained; the  $^{31}\text{P}$ -H coupled NMR spectra showed only broadened resonances for **3a,b**.

‡ Synthesis of **4a,b**: An ethereal solution (12 ml) of compound **2** (910 mg, 3.41 mmol) was added to a solution of  $(\text{CO})_5\text{M}=\text{C}(\text{OEt})\text{CH}_2\text{Li}$  **2a,b** (**2a**: 920 mg, 3.41 mmol; **2b**: 1373 mg, 3.41 mmol) in diethyl ether (40 ml) at  $-78^\circ\text{C}$ . After warming to room temperature (4 h), stirring was continued for 5 h. Separation of LiCl and removing the solvent *in vacuo* gave pale yellow solids, that were recrystallized from *n*-hexane (yield **4a**: 1450 mg, 86%, mp 118–119 $^\circ\text{C}$ ; yield **4b**: 1019 mg, 51%, mp 113–114 $^\circ\text{C}$ ).

§ NMR data were recorded at room temperature in  $\text{CDCl}_3$  solution at 50.3 MHz ( $^{13}\text{C}$ ) and 81.0 MHz ( $^{31}\text{P}$ );  $J/\text{Hz}$ . Selected spectroscopic data for **4a**:  $^{13}\text{C}$  NMR  $\delta$  91.22 [d,  $^1J_{\text{PC}}=99.06$ , C=P], 248.36 [d,  $^3J_{\text{PC}}=11.83$ , Cr=C];  $^{31}\text{P}$  NMR  $\delta$  -4.19 [ddquint,  $^1J_{\text{PH}}=534.99$ ,  $^2J_{\text{PH}}=24.25$ ,  $^3J_{\text{PH}}=6.05$ ];  $\text{M}^+$  at  $m/z = 494$ ; IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu/\text{cm}^{-1}$  2303(s), 2043(vs), 1972–1840(b), 1099(s), 983(vs), 898(s).

Selected data for **4b**:  $^{13}\text{C}$  NMR  $\delta$  94.03 [d,  $^1J_{\text{PC}}=98.08$ , C=P], 232.40 [d,  $^3J_{\text{PC}}=10.13$ , W=C];  $^{31}\text{P}$  NMR  $\delta$  -0.94 [ddquint,  $^1J_{\text{PH}}=535.27$ ,  $^2J_{\text{PH}}=24.10$ ,  $^3J_{\text{PH}}=6.11$ ];  $\text{M}^+$  at  $m/z = 626$ ; IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu/\text{cm}^{-1}$  2285(s), 2062(s), 1972(s), 1924(vs), 1261(vs), 1050(m), 894(s).

¶ Crystal data for **4a**:  $\text{C}_{21}\text{H}_{35}\text{CrN}_2\text{O}_6\text{P}$ , orthorhombic, *Pna*2<sub>1</sub>,  $a = 1518.5(6)$ ,  $b = 1021.0(4)$ ,  $c = 1721.5(8)$  pm,  $U = 2.669$  nm<sup>3</sup>,  $Z = 4$ ,  $\mu = 0.5$  mm<sup>-1</sup>,  $T = -100^\circ\text{C}$ . Yellow prism  $0.6 \times 0.6 \times 0.5$  mm, Mo-K $\alpha$

radiation, Siemens R3 diffractometer, 6482 intensities to  $2\theta_{\max}$  55°, 5249 unique ( $R_{\text{int}}$  0.058) used for all calculations. Structure solution by direct methods, anisotropic refinement on  $F^2$  (program SHELXL-93, G. M. Sheldrick, Univ. of Göttingen). Treatment of H atoms: PH free, rigid methyls, others riding. Final  $wR(F^2)$  0.153, conventional  $R(F)$  0.051 for 292 parameters. Full details may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the reference number CSD 401130, the names of the authors and the journal citation. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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