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Introduction of a phosphorus ylide moiety into [η²-(ω-hydroxy)alkenyl]chromium(0) carbene complexes with Ph_3PCCO and consecutive Wittig alkenations with 2-alkynals. Part 12: the chemistry of metallacyclic alkenylcarbene complexes ☆

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Abstract

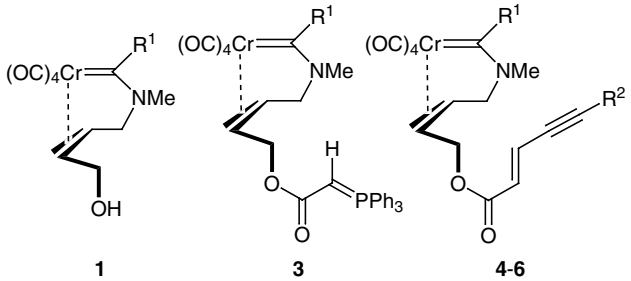
Ketenylidenetriphenylphosphorane, $Ph_3P{=}C{=}C{=}O$ (**2**), reacts selectively with the ω-hydroxy group of the alkene–carbene complexes $(OC)_4Cr{=}C(\eta^2\text{-}NMeCH_2CH{=}CHCH_2OH)R^1$ (**1**) (R^1 = Me: (**1a**); Ph: (**1b**)) to give the acyl ylide terminated complexes $(OC)_4Cr{=}C[(4,5\text{-}\eta^2)\text{-}NMeCH_2CH{=}CHCH_2O(O)C{-}CH{=}PPh_3]R^1$ (**3**) (R^1 = Me: (**3a**); Ph: (**3b**)). Complexes **3** undergo Wittig alkenation reactions with aldehydes such as 2-alkynals, $R^2{-}C{\equiv}C{-}CHO$ (R^2 = H, $SiMe_3$, Ph), to give the corresponding 4*Z*, 9*E*-dien-11-ynes $(OC)_4Cr{=}C[(4,5\text{-}\eta^2)\text{-}NMeCH_2CH{=}CHCH_2O(O)C{-}\mathit{CH}{=}\mathit{CH}{-}C{\equiv}C{-}R^2]R^1$ (**4–6**) (R^1 = Me, R^2 = H, $SiMe_3$, Ph: (**4a–6a**); R^1 = Ph, R^2 = H, $SiMe_3$, Ph: (**4b–6b**)). All complexes were characterized in solution by one- and two-dimensional NMR spectroscopy (^1H, ^{13}C, ^{29}Si, ^{31}P, $^1H/^1H$ COSY, $^{13}C/^1H$ HETCOR, $^{31}P/^{31}P$ EXSY).

Keywords: Chromium; Carbene complexes; η²-Alkene; Phosphorus ylides; Wittig alkenation; NMR

1. Introduction

Stable metallacyclic carbene–(η²-alkene) complexes of group VI transition metals [2–6] are ideal model systems for studying the sterical and electronical requirements and limitations of the elementary steps in olefin cyclopropanation [7–10] and metathesis [11–14] processes. They can in principle be fine-tuned by the choice of the central metal and of the ancillary ligands, and by adjusting the spatial orientation of the η²-bonded ligands via the length of the tether between them. To this end efficacious and selective ways to functionalize pre-formed such complexes are needed. For our current study of carbene–alkene–alkyne reaction cascades [15–19] potentially leading to metal-free oligo-heterocyclic frameworks "in one step", the introduction of additional olefin and acetylene residues was essential.

Herein, we describe the unprecedented introduction of an acyl phosphorus ylide group into (η²-alkene)chromiumcarbene complexes **1** through the reaction of a primary hydroxy group with the cumulated ylide $Ph_3P{=}C{=}C{=}O$ (**2**) [20] while not affecting the carbene nor the η²-alkene moieties. Subsequent Wittig olefination of the resulting chelate complexes **3** with unsaturated aldehydes furnished the desired chain-lengthened metallacycles **4–6**.



1 **3** **4-6**

☆ For Part 11, see [1].

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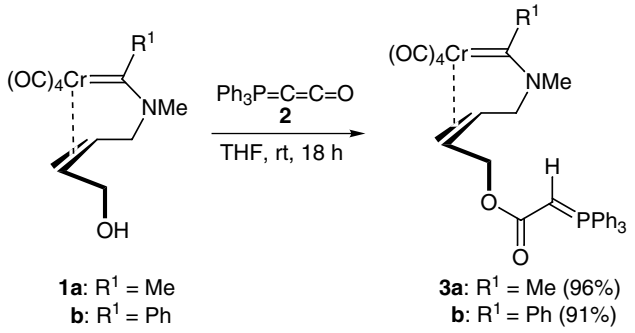
2. Results and discussion

2.1. Synthesis and properties of chelated (η^2-alkenyl)carbene complexes $(OC)_4Cr{=}C[(4,5\text{-}\eta^2)NMeCH_2CH{=}CHCH_2O_2C{-}CH{=}PPh_3]R^1$ (3)

Donor-substituted carbene complexes of tungsten [21] and chromium [22] react with various types of phosphorus ylides including **2** at the metal-bound carbene carbon atom. As η^2-coordinated alkenes and terminal CO ligands are also possible sites of attack of nucleophiles, it was gratifying to find ylide **2** reacting under very mild conditions selectively with the primary OH-group of **1** to give the corresponding yellow solid acyl ylides **3** in excellent yields (Scheme 1). Mechanistically, this process is likely [23] to commence with the protonation of the ylidic carbon atom C^{α} of **2** by the acidic OH-group of **1** to generate a very reactive ketenylium cation, $Ph_3P^{+}{-}HC^{\alpha}{=}C^{\beta}{=}O$, which in turn rapidly reacts with the conjugate alkoxide of **1** at its carbonyl carbon atom C^{β} furnishing the neutral ester ylide terminated complexes **3**. These can be obtained as pure, moderately air-stable crystal powders simply by washing and drying.

As is typical of most acyl ylides [24,25], compounds **3** exist as mixtures of *E*-isomers (**3**) and *Z*-isomers (**3′**) with respect to the PC–COO bond, a fact which is reflected in the ^{13}C and ^{31}P NMR spectra. Table 1 summarizes the ^{13}C NMR data of **3a/3a′** and **3b/3b′**, while ^{1}H NMR (and other analytical) data are detailed in Section 4. The ^{31}P NMR spectra of **3a/3a′** and **3b/3b′** show two signals



1a: R^1 = Me
b: R^1 = Ph

3a: R^1 = Me (96%)
b: R^1 = Ph (91%)

Scheme 1.

(ratio $E/Z = 2{:}1$) at 19.3 and 17.5 ppm, shifts typical of ester ylides. The line width of ca. 12 Hz indicated a slow exchange between the two species in solution at room temperature, which was further evidenced by the occurrence of strong cross-peaks in the $^{31}P/^{31}P$ EXSY (shown in Fig. 1 for **3a/3a′**) and the $^{1}H/^{1}H$ EXSY spectra.

2.2. Synthesis of chelated (η^2-alkadienynyl)carbene complexes $(OC)_4Cr{=}C[(4,5\text{-}\eta^2)NMeCH_2CH{=}CHCH_2O_2C{-}CH{=}CH{-}C{\equiv}C{-}R^2]R^1$ (4–6)

Ylide-terminated complexes **3** undergo clean Wittig alkenation reactions with aldehydes under surprisingly mild conditions (4–10 h, r.t.). Sterical shielding of the ylide portion by the alkene–carbene complex core is obviously neglectable. Being interested mainly in model

Table 1
^{13}C NMR data[a,b,c] of the complexes **3a/3a′** and **3b/3b′**

δ ^{13}C	M = C	=CH–	NMe	R^1	–CH_2–	CO	–CO_2–	–CH=P–	=PPh_3
		76.8 (s)			60.9 (s, C^{NCH_2})	225.5 (s)			128.8 (d, C^i) [92.0]
3a	274.2 (s)		38.5 (s)	33.4 (s, C^{Me})		226.4 (s)	171.4 (d) [14.7]	30.1 (d) [129.0]	129.7 (d, C^m) [12.1]
		83.2 (s)			62.1 (s, C^{CH_2O})	226.9 (s)			133.0 (d, C^p) [3.0]
						234.2 (s)			133.7 (d, C^o) [10.1]
		75.7 (s)			60.5 (s, C^{NCH_2})	225.7 (s)			129.5 (d, C^i) [91.7]
3a′	274.3 (s)		38.4 (s)	33.3 (s, C^{Me})		226.0 (s)	168.8 (d) [8.6]	29.6 (d) [136.0]	129.7 (d, C^m) [12.1]
		81.0 (s)			61.7 (s, C^{CH_2O})	227.0 (s)			132.7 (d, C^o) [9.9]
						234.3 (s)			133.2 (d, C^p) [3.0]
				119.8 (s, C^m)		224.7 (s)			128.6 (d,C^i) [91.5]
4a	274.9 (s)	77.4 (s)	41.3 (s)	126.5 (s, C^p)	60.8 (s, C^{NCH_2})	225.5 (s)	171.2 (d) [14.7]	30.3 (d) [129.1]	129.6 (d,C^i) [12.2]
		84.2 (s)		129.3 (s,C^o)	61.1 (s, C^{CH_2O})	227.4 (s)			133.0 (d, C^p) [2.6]
				149.4 (s, C^i)		232.1 (s)			133.7 (d, C^o) [10.0]
				119.6 (s, C^m)		224.8 (s)			129.2 (d, C^i) [91.5]
4a′	275.0 (s)	76.4 (s)	41.2 (s)	127.4 (s, C^p)	60.7 (s, C^{NCH_2})	226.0 (s)	169.2 (d) [8.4]	30.0 (d) [134.7]	129.7 (d, C^m) [12.0]
		82.1 (s)		129.1 (s, C^o)	61.9 (s, C^{CH_2O})	227.0 (s)			132.6 (d, C^o) [9.8]
				149.2 (s, C^i)		232.3 (s)			132.7 (d, C^p) [2.8]

[a] Solutions in acetone-d_6 (saturated; at 23 °C).
[b] Coupling constants $^nJ(^{31}P,^{13}C)$ are given in [ ] (±0.1 Hz).
[c] ^{31}P NMR: **3a/3a′** (2:1): δ = 19.3 (s), 17.5 (s); **4a/4a′** (2:1): δ = 19.3 (s), 17.5 (s).

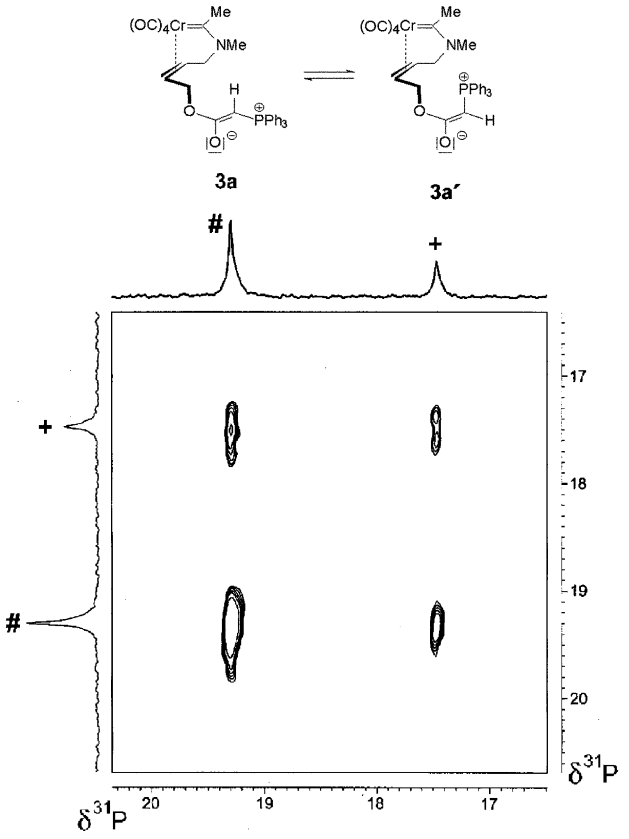
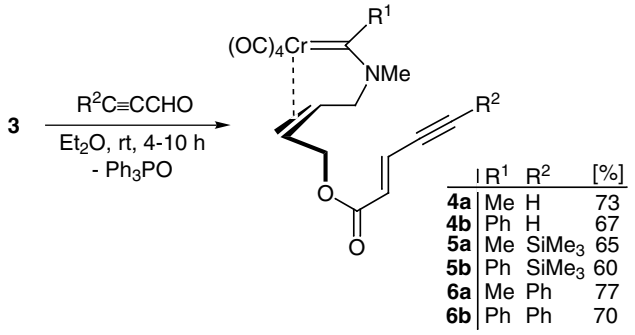


Fig. 1. $^{31}P/^{31}P$ EXSY spectrum of **3a** (#)/**3a′** (+) (saturated solution in acetone-d_6, recorded at 23 °C, mixing time: 0.2 s).

systems for domino alkene–alkyne–carbene processes we reacted exemplary 2-alkynals, R^2–C≡C–CHO with **3** to give the expected product complexes $(OC)_4$ Cr=C[(4,5-η^2)NMeCH$_2$CH=CHCH$_2$O$_2$C–CH=CH–C≡C–R^2]R^1 (**4**–**6**) as orangebrown, moderately air-stable powders in good yields (Scheme 2). These can be purified and separated from triphenylphosphane oxide, Ph_3PO, by filtration and consecutive flash chromatography (silica gel; diethyl ether). The newly formed double bond is predominantly *E*-configured (>98%) as to the coupling constant $^3J(^1H,^1H)$ of 15–16 Hz. Table 2 rehearses the



	R1	R2	[%]
4a	Me	H	73
4b	Ph	H	67
5a	Me	SiMe$_3$	65
5b	Ph	SiMe$_3$	60
6a	Me	Ph	77
6b	Ph	Ph	70

Scheme 2.

^{13}C NMR data of complexes **4**–**6**. Their structures were unambiguously assigned on grounds of $^1H/^1H$ COSY and $^{13}C/^1H$ HETCOR spectra (Fig. 2 depicts the latter of **4b**).

3. Conclusions

We have demonstrated that the established synthesis of *E*-α,β-unsaturated esters from alcohols, aldehydes and the cumulated ylide Ph_3PCCO [30] is also applicable to hydroxy functionalized alkene–carbene complexes of chromium. This should be a rather general method for the attachment of multiply functionalized side-chains to preformed carbene complexes via an ester linkage. We are currently investigating thermal intramolecular domino reactions of alkene–alkyne–carbene complexes **4**–**6**.

4. Experimental

4.1. General information

Preparation and handling of all compounds was carried out in an atmosphere of dry argon, and carefully dried solvents were used throughout. Starting materials were prepared according to the literature procedures, e.g., $(OC)_4Cr$=C(η^2-NMeCH$_2$CH=CHCH$_2$OH)R^1 (**1**) [1], Ph_3P=C=C=O [20], R^2–C≡C–CHO (R^2 = H [26], $SiMe_3$ [27], Ph [28]) or were used as purchased without further purification, e.g., HCO_2Et, Ph–C≡CH and R^2–C≡CCH$_2$OH (R^2 = H, $SiMe_3$).

NMR spectroscopy: Bruker ARX 250 and DRX 300 (^1H, ^{13}C, ^{29}Si, ^{31}P NMR); direct single pulse runs, or in case of the ^{29}Si NMR spectra by using the refocused INEPT pulse sequence with ^1H decoupling [29], based on $^2J(^{29}Si,^1H) \approx 7$ Hz. Chemical shifts are given with respect to Me_4Si [δ ^1H (CD_3COCD_2H) = 2.04; δ ^1H (C_6D_5H) = 7.15; δ ^{13}C (CD_3COCD_3) = 29.8, 204.0; δ ^{13}C (C_6D_6) = 128.0; δ ^{29}Si = 0 for Ξ (^{29}Si) = 19.867184 MHz] and external aqueous H_3PO_4 (85%) with δ ^{31}P = 0 for Ξ (^{31}P) = 40.480747 MHz. IR spectra: Perkin–Elmer, Spectrum 2000 FT-IR. EI-MS: Finnigan MAT 8500 (ionization energy 70 eV). Elemental analysis: Heraeus Mikromat C–H–N.

4.2. Synthesis of $(OC)_4Cr$=C[(4,5-η^2)NMeCH$_2$CH=CHCH$_2$O$_2$C–CH=PPh$_3$]R^1 (R^1 = Me: (**3a**); R^1 = Ph: (**3b**)) – general procedure

A solution of ketenylidenetriphenylphosphorane, Ph_3PCCO (**2**) (320 mg, 1.06 mmol) in THF (10 ml) was added to a solution of $(OC)_4Cr$=C(η^2-NMeCH$_2$CH=CHCH$_2$OH)R^1 (R^1 = Me: (**1a**); R^1 = Ph: (**1b**)) (1.00 mmol) and 3 mg of benzoic acid in the same sol-

Table 2
^{13}C NMR data[a] of the complexes **4**, **5**[b] and **6**

δ ^{13}C	M=C	=CH–	NMe	R^1	$-CH_2-$	CO	$-CO_2-$	*E*-CH=CH	$-C\equiv C-$	R^2
4a	277.5 (s)	73.5 (s)		32.9 (s)	61.3 (s, C^{NCH_2})	218.2 (s)			80.2 (s)	–
			36.6 (s)			224.5 (s)	165.0 (s)	124.6 (s)		
		75.7 (s)			64.4 (s, C^{CH_2O})	225.3 (s)		132.5 (s)	87.0 (s)	
						232.9 (s)				
4b	278.6 (s)	74.3 (s)		119.7 (s, C^m)	60.4 (s, C^{NH2})	223.7 (s)			80.2 (s)	–
			39.8 (s)	126.7 (s, C^p)		224.2 (s)	165.1 (s)	124.8 (s)		
		76.8 (s)		128.7 (s, C^o)	64.4 (s, C^{CH_2O})	226.6 (s)		132.5 (s)	87.1 (s)	
				148.4 (s, C^i)		230.5 (s)				
5a	277.2 (s)	73.7 (s)		32.9 (s)	61.3 (s, C^{NCH_2})	218.2 (s)			101.8 (s)	−0.5 (s, C^{Me}) {56.8}
			36.7 (s)			224.5 (s)	165.3 (s)	125.6 (s)		
		76.0 (s)			64.3 (s, C^{CH_2O})	225.4 (s)		131.4 (s)	105.7 (s)	
						233.0 (s)				
5b	278.3 (s)	74.4 (s)		118.8 (s, C^m)	60.5 (s, C^{NCH_2})	223.8 (s)			101.9 (s)	−0.6 (s, C^{Me}) {56.5}
			39.8 (s)	125.9 (s, C^p)		224.3 (s)	165.4 (s)	128.7 (1s)		
		77.1 (s)		129.4 (s, C^o)	64.3 (s, C^{CH_2O})	226.6 (s)		131.3 (s)	105.9 (s)	
				148.5 (s, C^i)		230.7 (s)				
6a	277.0 (s)	74.1 (s)		33.0 (s)	61.3 (s, C^{NCH_2})	218.2 (s)			86.8 (s)	122.4 (s, C^i)
			36.9 (s)			224.4 (s)	165.4 (s)	129.1 (s)		125.7 (s, C^m)
		76.6 (s)			64.3 (s, C^{CH_2O})	225.5 (s)		133.6 (s)	99.4 (s)	130.1 (s, C^p)
						233.0 (s)				132.2 (s, C^o)
6b	278.4 (s)	74.5 (s)		118.8 (s, C^m)	60.4 (s, C^{NCH_2})	223.7 (s)			86.9 (s)	122.5 (s, C^i)
			39.9 (s)	126.7 (s, C^p)		224.3 (s)	165.6 (s)	128.7 (s)		125.9 (s, C^m)
		77.3 (s)		129.6 (s, C^o)	64.3 (s, C^{CH_2O})	226.6 (s)		132.2 (s)	99.5 (s)	130.1 (s, C^p)
				148.5 (s, C^i)		230.6 (s)				133.2 (s, C^o)

[a] Solutions in acetone-d_6 (saturated; at 23 °C).
[b] ^{29}Si NMR: **5a**: $\delta = -16.6$ (s); **5b**: $\delta = -16.6$ (s); coupling constants $^nJ(^{29}Si,^{13}C)$ are given in { } (±0.1 Hz).

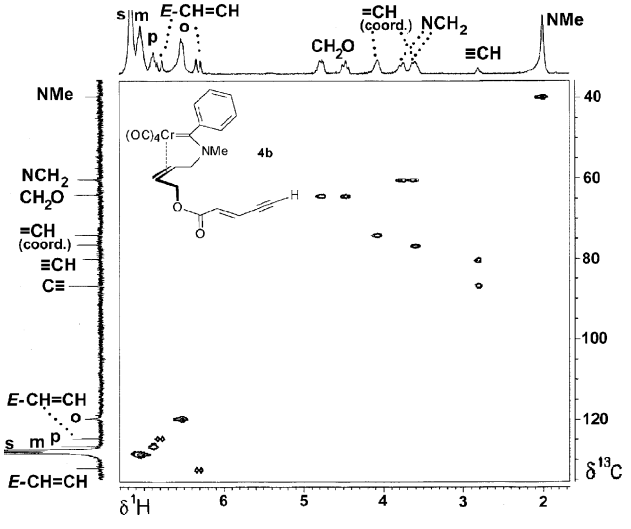


Fig. 2. $^{13}C/^1H$ HETCOR NMR spectrum of **4b** (saturated solution in C_6D_6 (s), run at 23 °C): the additional cross-peak for the internal alkyne carbon is due to the large $^2J(^{13}C^{\equiv C},^1H)$ coupling.

vent (20 ml). The resulting mixture was stirred at room temperature for 18 h and the solvent was then removed in vacuo. The residue thus obtained was washed several times with small portions of pentane and dried in vacuo to give the products **3** as yellow powders.

4.2.1. $(OC)_4Cr{=}C[(4,5\text{-}\eta^2)NMeCH_2CH{=}CHCH_2O_2\text{-}C\text{–}CH{=}PPh_3]Me$ (**3a**/**3a′**)

M.p. 46 °C (dec.), yield: 570 mg (96%). ^1H NMR (300.13 MHz, acetone-d_6, 23 °C): **3a**: $\delta = 2.32$ (s, 3H, H^{Me}), 2.90 [d, 1H, $^2J(^{31}P,^1H) = 23.0$ Hz, $H^{CH=P}$], 3.06 (s, 3H, H^{NMe}), 3.95 (m, 1H, $H^{=CH}$), 4.16 (m, 1H, H^{NCH_2}), 4.38 (m, 2H, H^{CH_2O}), 4.54 (m, 1H, H^{NCH_2}), 4.62 (m, 1H, $H^{=CH}$), 7.57–7.72 (m, 15H, Ph); **3a′**: $\delta = 2.25$ (s, 3H, H^{Me}), 2.52 [d, 1H, $^2J(^{31}P,^1H) = 22.0$ Hz, $H^{CH=P}$], 3.03 (s, 3H, H^{NMe}), 3.32 (m, 1H, $H^{=CH}$), 3.56 (m, 2H, H^{NCH_2}), 3.83 (m, 1H, H^{CH_2O}), 3.77 (m, 1H, H^{CH_2O}), 4.25 (m, 1H, $H^{=CH}$), 7.57–7.72 (m, 15H, Ph). IR (ATR) 2051/2003/1883/1850 cm^{-1} [ν(Cr(CO)$_4$)], 1628 [ν(C=O)], 1549 [ν(C=C)], 1436 [ν(P–Ph)], 1101 [ν(C–O)]. EI-MS: m/z (%) = 398 (9), 314 (43), 277 (100) [$Ph_3PCH_3^+$], 262 (34) [PPh_3^+], 252 (29), 201 (27), 183 (53), 157 (9), 110 (9), 77 (18), 52 (27) [Cr^+]. Anal. Calc. for $C_{31}H_{28}CrNO_6P$ (593.1) C, 63.73; H, 4.76; N 2.36. Found: C, 63.26; H, 5.01; N, 2.49%.

4.2.2. $(OC)_4Cr{=}C[(4,5\text{-}\eta^2)NMeCH_2CH{=}CHCH_2O_2\text{-}C\text{–}CH{=}PPh_3]Ph$ (**3b**/**3b′**)

M.p. 57 °C (dec.), yield: 597 mg (91%). ^1H NMR (250.13 MHz, acetone-d_6, 23 °C): **3b**: $\delta = 2.88$ (s, 3H, H^{NMe}), 3.03 [d, 1H, $^2J(^{31}P,^1H) = 22.5$ Hz, $H^{CH=P}$], 3.39 (m, 1H, H^{NCH_2}), 3.61 (m, 1H, H^{CH_2O}), 4.07 (m, 1H,

$H^{=CH}$), 4.51 (m, 1H, H^{CH_2O}), 4.61 (m, 1H, H^{NCH_2}), 4.82 (m, 1H, $H^{=CH}$), 6.80 (m, 2H, H^o), 7.18 (m, 1H, H^p), 7.37 (m, 2H, H^m), 7.57–7.76 (m, 15H, PPh_3); **3b′**: $\delta = 3.05$ (s, 3H, H^{NMe}), 2.55 [d, 1H, $^2J(^{31}P,^1H) = 21.8$ Hz, $H^{CH=P}$], 3.86 (s, 1H, $H^{=CH}$), 4.21 (m, 1H, H^{NCH_2}), 4.36 (m, 1H, H^{CH_2O}), 4.45 (m, 1H, H^{CH_2O}), 4.65 (m, 1H, H^{NCH_2}), 4.88 (m, 1H, $H^{=CH}$), 6.73 (m, 2H, H^o), 7.18 (m, 1H, H^p), 7.40 (m, 2H, H^m), 7.57–7.76 (m, 15H, PPh_3). IR (ATR) 2052/2005/1896/1862 cm^{-1} [$\nu(Cr(CO)_4)$], 1616 [$\nu(C{=}O)$], 1540 [$\nu(C{=}C)$], 1437 [$\nu(P–Ph)$], 1102 [(C–O)]. EI-MS: m/z (%) = 398 (1), 314 (24), 277 (100) [$Ph_3PCH_3^+$], 262 (3) [PPh_3^+], 221 (9), 201 (25), 183 (19), 170 (21), 118 (11), 108 (22), 91 (9), 77 (28), 52 (57) [Cr^+]. Anal. Calc. for $C_{36}H_{30}CrNO_6P$ (655.6) C, 65.95; H, 4.61; N 2.14. Found: C, 65.96; H, 4.82; N, 2.39%.

*4.3. Synthesis of (OC)$_4$Cr=C[(4,5-η^2)NMeCH$_2$CH=CHCH$_2$O$_2$C–CH=CH–C≡C–R^2]R^1 (R^1 = Me, R^2 = H: (**4a**), R^2 = SiMe$_3$: (**5a**), R^2 = Ph: (**6a**); R^1 = Ph, R^2 = H: (**4b**), R^2 = SiMe$_3$: (**5b**), R^2 = Ph: (**6b**)) – general procedure*

The 2-alkynal, R^2–C≡C–CHO (R^2 = H, $SiMe_3$, Ph; 1.3 mmol), was dissolved in diethyl ether (10 ml) and added to a solution of **3** (1.0 mmol) in the same solvent (30 ml). The resulting mixture was stirred at room temperature for several hours whereupon a fine white precipitation was formed and the color of the solution turned dark. All volatiles were removed on a rotary evaporator and the residue was taken up in diethyl ether (50 ml). The solution thus obtained was filtered and flash-chromatographed over a short column (silica gel, diethyl ether) to remove Ph_3PO. The eluate was concentrated to dryness, the remainder was washed several times with pentane and finally recrystallized from toluene and dried in vacuo to give **4**–**6** as brown powders.

*4.3.1. (OC)$_4$Cr=C[(4,5-η^2)NMeCH$_2$CH=CHCH$_2$O$_2$C–CH=CH–C≡CH]Me (**4a**)*

M.p. 110 °C (dec.), yield: 270 mg (73%) from propynal (55 mg) and **3a**, reaction time 4 h. ^{1}H NMR (300.13 MHz, C_6D_6, 23 °C): $\delta = 1.71$ (s, 3H, H^{Me}), 1.86 (s, 3H, H^{NMe}), 2.81 (s, 1H, $H^{\equiv CH}$), 3.50 (m, 1H, $H^{=CH}$), 3.53 (m, 1H; H^{CH_2N}), 3.59 (m, 1H, H^{NCH_2}), 3.90 (m, 1H, $H^{=CH}$), 4.10 (m, 1H, H^{CH_2O}), 4.64 (m, 1H, H^{CH_2O}), 6.29 (d, 1H, $^3J(^1H,^1H) = 15.9$ Hz, $H^{COCH=}$), 6.78 (d, 1H, $^3J(^1H,^1H) = 15.9$ Hz, $H^{=CH}$). IR (ATR): 2196 cm^{-1} [$\nu(C{\equiv}C)$], 2051/2009/1902/1884 [$\nu(Cr(CO)_4)$], 1709 [$\nu(C{=}O)$], 1615 [$\nu(C{=}C)_E$], 1525 [$\nu(C{=}C)_{coord.}$], 1259 [$\nu(C–O)$]. EI-MS: m/z (%) = 369 (3) [M^+], 359 (9), 347 (11), 341 (3) [M^+–CO], 313 (3) [M^+–2CO], 308 (15), 285 (9) [M^+–3CO], 277(49), 257 (20) [M^+–4CO], 215 (35), 165 (35), 152 (29), 115 (61), 91 (81), 77 (100), 52 (54) [Cr^+], 44 (97), 28 (33) [CO^+]. Anal. Calc. for $C_{16}H_{15}CrNO_6$ (369.3) C, 52.04; H, 4.09; N 3.79. Found: C, 51.94; H, 4.15; N, 3.69%.

*4.3.2. (OC)$_4$Cr=C[(4,5-η^2)NMeCH$_2$CH=CHCH$_2$O$_2$C–CH=CH–C≡CH]Ph (**4b**)*

M.p. 115 °C (dec.), yield: 289 mg (67%) from propynal (55 mg) and **3b**, reaction time 4 h. ^{1}H NMR (250.13 MHz, C_6D_6, 23 °C): $\delta = 1.96$ (s, 3H, H^{NMe}), 2.80 (d, 1H, $^4J(^1H,^1H) = 1.6$ Hz; $H^{\equiv CH}$), 3.58 (m, 1H, $H^{=CH}$), 3.60 (m, 1H, H^{NCH_2}), 3.74 (m, 1H, H^{NCH_2}), 4.05 (m, 1H, $H^{=CH}$), 4.45 (m, 1H, H^{CH_2O}), 4.77 (m, 1H, H^{CH_2O}), 6.32 (d, 1H, $^3J(^1H,^1H) = 15.6$ Hz, $H^{COCH=}$), 6.51 (m, 2H, H^o), 6.81 (dd, 1H, $^3J(^1H,^1H) = 15.6$ Hz, $^4J(^1H,^1H) = 1.6$ Hz; $H^{=CH}$), 6.87 (m, 1H, H^p), 7.03 (m, 2H, H^m). IR (ATR): 2189 cm^{-1} [$\nu(C{\equiv}C)$], 2053/2008/1862 [$\nu(Cr(CO)_4)$], 1713 [$\nu(C{=}O)$], 1619 [$\nu(C{=}C)_E$], 1538 [$\nu(C{=}C)_{coord.}$], 1259 [$\nu(C–O)$]. EI-MS: m/z (%) = 431 (1) [M^+], 375 (1) [M^+–2CO], 347 (1) [M^+–3CO], 319 (2) [M^+–4CO], 308 (10), 262 (18), 244 (19), 207 (35), 170 (32), 155 (33), 118 (63), 91 (100) [$C_7H_7^+$], 77 (50) [$C_6H_6^+$], 52 (46) [Cr^+]. Anal. Calc. for $C_{21}H_{17}CrNO_6$ (431.4) C, 58.47; H, 3.97; N 3.26. Found: C, 58.65; H, 3.83; N, 3.15%.

*4.3.3. (OC)$_4$Cr=C[(4,5-η^2)NMeCH$_2$CH=CHCH$_2$O$_2$C–CH=CH–C≡CSiMe$_3$]Me (**5a**)*

M.p. 69 °C (dec.), yield: 286 mg (65%) from $Me_3SiC{\equiv}CCHO$ (127 mg) and **3a**, reaction time 7 h. ^{1}H NMR (300.13 MHz, C_6D_6, 23 °C): $\delta = 0.13$ (s, 9H, H^{SiMe_3}), 1.71 (s, 3H, H^{Me}), 1.89 (s, 3H, H^{NMe}), 3.47 (m, 1H, $H^{=CH}$), 3.50 (m, 1H; H^{NCH_2}), 3.59 (m, 1H, H^{NCH_2}), 3.90 (m, 1H, $H^{=CH}$), 4.06 (m, 1H, H^{CH_2O}), 4.63 (m, 1H, H^{CH_2O}), 6.31 (d, 1H, $^3J(^1H,^1H) = 15.8$ Hz, $H^{COCH=}$), 6.92 (d, 1H, $^3J(^1H,^1H) = 15.8$ Hz, $H^{=CH}$). IR (ATR): 2169 cm^{-1} [ν (C≡C)], 2053/2010/1894/1869 [$\nu(Cr(CO)_4)$], 1712 [$\nu(C{=}O)$], 1617 [$\nu(C{=}C)_E$], 1542 [$\nu(C{=}C)_{coord.}$], 1255 [$\nu(SiMe_3)$], 1249 [$\nu(C–O)$]. EI-MS: m/z (%) = 441 (4) [M^+], 413 (1) [M^+–CO], 385 (1) [M^+–2CO], 357 (5) [M^+–3CO], 329 (49) [M^+–4CO], 314 (9), 301 (8), 260 (14), 225 (20), 220 (28), 182 (17), 151 (100), 126 (89), 108 (78), 91 (73), 83 (61), 73 (57) [$SiMe_3^+$], 52 (58) [Cr^+]. Anal. Calc. for $C_{19}H_{23}CrNO_6Si$ (441.5) C, 51.69; H, 5.25; N 3.19. Found: C, 51.76; H, 5.37; N, 3.07%.

*4.3.4. (OC)$_4$Cr=C[(4,5-η^2)NMeCH$_2$CH=CHCH$_2$O$_2$C–CH=CH–C≡CSiMe$_3$]Ph (**5b**)*

M.p. 76 °C (dec.), yield: 302 mg (60%) from $Me_3SiC{\equiv}CCHO$ (127 mg) and **3b**, reaction time 10 h. ^{1}H NMR (250.13 MHz, C_6D_6, 23 °C): $\delta = 0.27$ (s, 9H, H^{SiMe_3}), 2.00 (s, 3H, H^{NMe}), 3.58 (m, 1H, H^{NCH_2}), 3.62 (m, 1H; $H^{=CH}$), 3.83 (m, 1H, H^{NCH_2}), 4.07 (m, 1H, $H^{=CH}$), 4.44 (m, 1H, H^{CH_2O}), 4.77 (m, 1H, H^{CH_2O}), 6.37 (d, 1H, $^3J(^1H,^1H) = 15.7$ Hz, $H^{OCCH=}$), 6.51 (m, 2H, H^o), 6.88 (m, 1H, H^p), 6.91 (d, 1H, $^3J(^1H,^1H) = 15.7$ Hz, $H^{=CH}$), 7.03 (m, 2H, H^m). IR (ATR) 2170 cm^{-1} [$\nu(C{\equiv}C)$], 2053/2010/1908/1873 [$\nu(Cr(CO)_4)$], 1712 [$\nu(C{=}O)$], 1616 [$\nu(C{=}C)_E$], 1540 [$\nu(C{=}C)_{coord.}$], 1253 [$\nu(SiMe_3)$], 1249 [$\nu(C–O)$]. EI-MS: m/z (%) = 503 (1) [M^+], 475 (1) [M^+–CO], 447 (3) [M^+–2CO], 391 (7) [M^+–4CO], 313 (6), 225 (13), 170 (100), 118 (14), 105

(11), 73 (14), 52 (21) [Cr+]. Anal. Calc. for $C_{24}H_{25}CrNO_6Si$ (503.5) C, 57.25; H, 5.00; N 2.79. Found: C, 57.38; H, 4.91; N, 2.68%.

4.3.5. $(OC)_4Cr{=}C[(4,5\text{-}\eta^2)NMeCH_2CH{=}CHCH_2O_2\text{-}C\text{–}CH{=}CH\text{–}C{\equiv}CPh]Me$ (**6a**)

M.p. 94 °C (dec.), yield: 343 mg (77%) from phenylpropynal (130 mg) and **3a**, reaction time 6 h. ^{1}H NMR (250.13 MHz, C_6D_6, 23 °C): $\delta = 1.85$ (s, 3H, H^{Me}), 2.02 (s, 3H, H^{NMe}), 3.54 (m, 1H, $H^{=CH}$), 3.59 (m, 1H, H^{NCH_2}), 3.70 (m, 1H; H^{NCH_2}), 3.83 (m, 1H, $H^{=CH}$), 4.28 (m, 1H, H^{CH_2O}), 4.82 (m, 1H, H^{CH_2O}), 6.54 (d, 1H, $^3J(^1H,^1H) = 15.7$ Hz, $H^{OCCH=}$), 7.12 (m, 2H, H^m), 7.32 (d, 1H, $^3J(^1H,^1H) = 15.7$ Hz, $H^{=CH}$), 7.51 (m, 1H, H^p), 7.89 (m, 2H, H^o). IR (ATR): 2198 cm^{-1} [ν(C≡C)], 2052/2007/1894/1858 [$\nu(Cr(CO)_4)$], 1706 [ν(C=O)], 1616 [$\nu(C{=}C)_E$], 1543 [$\nu(C{=}C)_{coord.}$], 1248 [ν(C–O)]. EI-MS: m/z (%) = 445 (1) [M$^+$], 417 (2) [M$^+$–CO], 389 (2) [M$^+$–2CO], 361 (2) [M$^+$–3CO], 333 (4) [M$^+$–4CO], 323 (5), 308 (10), 270 (9), 244 (13), 204 (13), 170 (28), 156 (34), 115 (26), 91 (100), 77 (42), 52 (26) [Cr$^+$]. Anal. Calc. for $C_{22}H_{19}CrNO_6$ (445.4) C, 59.33; H, 4.30; N 3.16. Found: C, 59.19; H, 4.34; N, 3.11%.

4.3.6. $(OC)_4Cr{=}C[(4,5\text{-}\eta^2)NMeCH_2CH{=}CHCH_2O_2\text{-}C\text{–}CH{=}CH\text{–}C{\equiv}CPh]Ph$ (**6b**)

M.p. 102 °C (dec.), yield: 355 mg (70%) from phenylpropynal (130 mg) and **3b**, reaction time 7 h. ^{1}H NMR (250.13 MHz, C_6D_6, 23 °C): $\delta = 2.01$ (s, 3H, H^{NMe}), 3.65 (m, 1H; $H^{=CH}$), 3.81 (m, 1H, H^{NCH_2}), 4.10 (m, 1H, $H^{=CH}$), 4.33 (m, 1H, H^{NCH_2}), 4.63 (m, 1H, H^{CH_2O}), 4.82 (m, 1H, H^{CH_2O}), 6.43 (d, 1H, $^3J(^1H,^1H) = 15.6$ Hz, $H^{OCCH=}$), 6.52 (m, 2H, H^o), 6.80–7.65 (m,m,m,m, 9H, H^{Ph}/$H^{=CHC}$). IR (ATR): 2198 cm^{-1} [ν(C≡C)], 2054/2008/1884/1858 [$\nu(Cr(CO)_4)$], 1710 [ν(C=O)], 1617 [$\nu(C{=}C)_E$], 1543 [$\nu(C{=}C)_{coord.}$], 1258 [ν(C–O)]. EI-MS: m/z (%) = 507 (1) [M$^+$], 479 (1) [M$^+$–CO], 451 (1) [M$^+$–2CO], 423 (2) [M$^+$–3CO], 395 (3) [M$^+$–4CO], 373 (6), 347 (9), 297 (11), 271 (27), 244 (49), 202 (31), 165 (35), 152 (24), 118 (47), 91 (100) [$C_7H_7^+$], 77 (73) [$C_6H_6^+$], 52 (44) [Cr$^+$]. Anal. Calc. for $C_{27}H_{21}CrNO_6$ (507.5) C, 63.91; H, 4.17; N 2.77. Found: C, 64.08; H, 4.06; N, 2.61%.

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