Transition Met. Chem., **20**, 508–510 (1995)

Synthesis and structural characterization of tricarbonyl *bis*-[Di(*N*,*N*″-allylamino)carbene]chromium and tungsten(0) complexes

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Summary

The reaction *in situ* of $[\mathrm{M(CO)_6}]$ (M = Cr or W), 1,2-*bis*(*N*-allylamino)ethane and $\mathrm{CH(NMe_2)(OMe)_2}$ has resulted in the isolation of chelated metal carbene compounds in low yield. A [3,3] amino-Claisen rearrangement of a transient allyl electron-rich olefin, the organic precursor of the carbenes, appears to be the principal product. A single crystal X-ray diffraction study has shown that the tungsten complex has similar structural parameters to a molybdenum–carbene previously communicated. Detailed characterization of family six (G, No, W) chelated carbene compounds has been completed.

Introduction

In 1970 Chauvin and Hérisson(1) first suggested that carbene–olefin intermediates were included in olefin metathesis. These compounds are also proposed as intermediates in cyclopropanation(2), Fischer–Tropsch(3) and Ziegler–Natta(4) catalytic processes. In a theoretical analysis of the possible geometries that a metal–carbene–olefin can adopt, Hoffmann *et al.*(5) concluded that only one conformation, where both ligand functions are coplanar and share the same t_{2g} orbital of the metal, will undergo metathesis or cyclopropanation. This prediction has been proved experimentally(6), however compounds where both ligand functions are perpendicular with stronger experimental conditions gave the cyclopropanation product(7).

Prior to this work, only the molybdenum carbene–olefin complex derived from electron-rich olefins had been characterized. With these two new compounds, information of all carbene–olefins of family six is available.

Experimental

Reactions were routinely carried using standard Schlenk line procedures under Ar and using dry $\mathrm{O_2}$-free solvents. The compound $\mathrm{H_5C_3NH(C_2H_4)HNC_3H_5}$ was prepared by published procedures(8). $[\mathrm{M(CO)_6}]$ (M = Cr or W) and DMF-dimethyl acetal (Aldrich Chemical Co.) were used as received. I.r. spectra were recorded as $\mathrm{CH_2Cl_2}$ solutions or on CsI plates using a Perkin-Elmer 1330 spectrometer. Solution room temperature ^{1}H- and ^{13}C{^{1}H}-n.m.r. spectra were recorded using a Varian VXR-300 MHz spectrometer externally referenced to TMS (299.94 and 75.42 MHz, respectively). Mass spectra were registered in 5985 Hewlett Packard spectrometer through the electronic impact technique.

Synthesis of $[(\mathrm{OC})_4\mathrm{W{=}CN(CH_2CH{=}CH_2)}$-$\mathrm{CH_2CH_2N(CH_2CH{=}CH_2)}]$ [(3a)]

A mixture of $[\mathrm{W(CO)_6}]$ (4.22 g, 12 mmol), 1,2-*bis*(allylamino)ethane (1.68 g, 12 mmol) and $\mathrm{CH(NMe_2)}$-$\mathrm{(OMe)_2}$ (1.57 g, 13 mmol) in decaline was boiled under reflux for 3 h. Unchanged solid $[\mathrm{W(CO)_6}]$ was then removed by filtration. Volatiles with traces of $[\mathrm{W(CO)_6}]$ were evaporated *in vacuo* from the filtrate. The residual yellow oil was dissolved in $\mathrm{Et_2O}$–hexane. Yellow crystals of the compound (0.11 g, 3.7%) separated when the solution was kept at −30 °C (Found: C, 33.1; H, 3.3; N, 5.9; $\mathrm{C_{13}H_{14}N_2O_4W}$ calcd.: C, 34.9; H, 3.1; N, 6.2%). I.r. (KBr) $\nu(\mathrm{CN_2})$ 1500, ν(CO) 2018, 1910, 1860 cm^{-1}. N.m.r. {^{1}H} (299.94 MHz, $\mathrm{CDCl_3}$) δ (p.p.m.) 5.7–5.8 (m, 1H, $\mathrm{CH{=}CH_2}$), 5.2 (m, 2H $\mathrm{CH_2{=}CH}$—), 3.1–3.3 [m, 4H, $\mathrm{N(CH_2)_2N}$]; RMN ^{13}C{^{1}H} (75.42 MHz, $\mathrm{CDCl_3}$) δ (p.p.m.) 216.8 (C carbene), 216.05 (CO *trans*), 205.60 and 204.85 (CO *cis*), 56.7 (coordinated $\mathrm{CH_2{=}}$*CH*—), 75.2 (coordinated CH=*CH*$_2$), 208.50 (CO *trans*), 118.0 (free $\mathrm{CH_2{=}}$*CH*—), 134.1 (free CH=*CH*$_2$), 49.9, 49.2 ($\mathrm{N(CH_2)_2N}$. Mass spectra, *m*/*z* 446 (M$^+$).

Synthesis of $[(\mathrm{OC})_4\mathrm{Cr{=}CN(CH_2CH{=}CH_2)}$-$\mathrm{CH_2CH_2N(CH_2CH{=}CH_2)}]$ [(3b)]

The same procedure as above was employed and yellow crystals were obtained (0.22 g, 10.9%) (Found: C, 49.5; H, 4.7; N, 8.8; $\mathrm{C_{13}H_{14}N_2O_4Cr}$ calcd.: C, 49.6; H, 4.4; N, 8.9%). I.r. ($\mathrm{CH_2Cl_2}$, CsI) $\nu(\mathrm{CN_2})$ 1500 cm^{-1}, ν(CO) 2018, 1920, 1885 cm^{-1}. N.m.r. {^{1}H} (299.94 MHz, $\mathrm{C_6D_6}$) δ (p.p.m.) 5.5–5.7 (m, 1H, $\mathrm{CH{=}CH_2}$), 4.9 (m, 2H, $\mathrm{CH_2{=}CH}$—), 2.5–2.1 [m, 4H, $\mathrm{N(CH_2)_2N}$]; RMN ^{13}C{^{1}H} (75.42 MHz, $\mathrm{C_6H_6}$) δ (p.p.m.) 235.1 (C carbene), 229.12 (CO *trans*), 226.63 and 224.29 (CO *cis*), 63.5 (coordinated $\mathrm{CH_2{=}}$*CH*—), 80.0 (coordinated CH=*CH*$_2$), 227.79 (CO *trans*), 117.8 (free $\mathrm{CH_2{=}}$*CH*—), 133.3 (free CH=*CH*$_2$), 49.4, 47.6 ($\mathrm{N(CH_2)_2N}$. Mass spectra, *m*/*z* 314 (M$^+$).

Crystal structure determination of (3a)

Yellow crystals of *(3a)* were grown by slow diffusion of hexane into a $\mathrm{CH_2Cl_2}$ solution of the compound. A single crystal of dimensions 0.4 × 0.18 × 0.32 mm was mounted on a glass fibre and transferred to a Nicolet-P3 diffractometer. Final unit cell dimensions, calculated from a least-squares treatment of angles of 25 accurately centred reflections are given in Table 1. A total of 2147 reflections were collected using $\omega/2\theta$ scans $(2^\circ + (K_{\alpha_1} - K_{\alpha_2})$ using graphite-monochromated MoK_α radiation, of which 2041 were unique and 1623 considered observed ($F > 3\sigma(F)$, $R_{\mathrm{merg}} = 0.063$). Data were corrected by *Lp* and absorption (DIFABS)(9). The structure was solved by the 'heavy atom' method. All non-hydrogen atoms refined anisotropically (H-atoms at idealized

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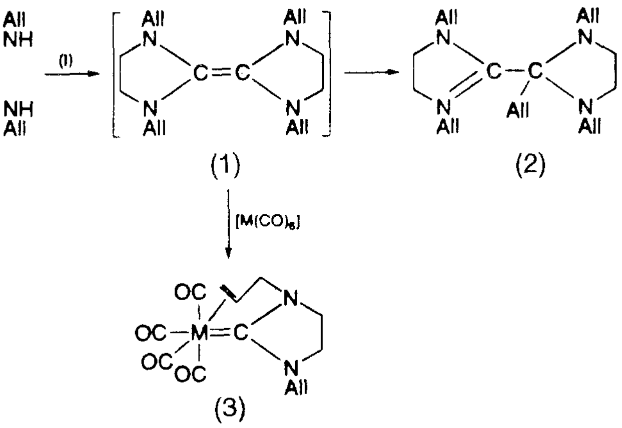
Table 1. Summary of data collection and structure solution of *(3a)*

Compound	$C_{13}H_{14}WN_2O_4$
Mol. wt.	446.11
Crystallographic system	monoclinic
Space group	$P2_1/n$
Cell dimensions (Å)	$a = 7.861(3)$
	$b = 16.385(5)$ $\beta = 101.83(2)$
	$c = 11.686(3)$
Cell volume (Å^3)	1473(1)
Z	4
Density (g cm^{-3})	2.011
μ (cm^{-1})	82.97
Radiation	MoK_α ($\lambda = 0.71073$ Å)
Decay of standards	$\pm 3\%$
2θ Range (octants) (°)	3–50 (*hkl, hk – l*)
Reflections used	1623 [$F > 3\sigma(F)$]
Secondary extinction	0.0005(1)
Weighting scheme	$1/\sigma^2(F) + 0.002989\ F^2$
rms shift/esd	0.01222
Number of parameters varied	182
R	0.047
R_w	0.051

positions) by full-matrix least-squares based on the F observed magnitudes. Information was processed on a PC computer using SHELXTL program. Scattering factors can be found elsewhere(10). Refinement converged with $R = 0.047$ and $R_w = 0.051$.

Results and discussion

The compounds were obtained by the reaction *in situ* of the corresponding electron-rich olefin and the metal carbonyl reagent (Scheme 1). Different attempts to isolate *(1)* by the reaction of N,N-dimethylformamide dimethylacetal with the corresponding secondary diamine (the usual procedure to obtain electron-rich olefins) failed, due to its facile [3, 3] sigmatropic amino-Claisen rearrange-



Scheme 1. Synthesis of N-functionalized carbene–transition metal(0) carbonyls; *(3a)* = W, *(3b)* = Cr. Reagents and conditions: (i) CH(NMe$_2$)(OMe)$_2$, decaline, 1.5 h and distilled (–2MeOH, –Me$_2$NH).

Table 2. Selected bond lengths (Å) and angles (°) of *(3a)* with e.s.d.s in parentheses

Bond lengths			
W—C(1)	2.01(1)	W—C(2)	1.98(1)
W—C(3)	1.97(2)	W—C(4)	2.05(1)
W—C(5)	2.21(1)	W—C(12)	2.41(1)
W—C(13)	2.41(1)	C(1)—O(1)	1.17(2)
C(2)—O(2)	1.16(2)	C(3)—O(3)	1.18(2)
C(4)—O(4)	1.12(2)	N(1)—C(5)	1.33(2)
N(1)—C(7)	1.47(2)	N(1)—C(8)	1.43(2)
C(5)—N(2)	1.33(2)	N(2)—C(6)	1.48(2)
N(2)—C(11)	1.46(2)	C(6)—C(7)	1.56(3)
C(8)—C(9)	1.56(2)	C(9)—C(10)	1.31(2)
C(11)—C(12)	1.52(2)	C(12)—C(13)	1.36(2)
Bond angles			
C(1)—W—C(2)	86.1(5)	C(1)—W—C(3)	86.8(5)
C(2)—W—C(3)	92.4(6)	C(1)—W—C(4)	171.5(5)
C(2)—W—C(4)	90.2(5)	C(3)—W—C(4)	85.8(5)
C(1)—W—C(5)	90.3(4)	C(2)—W—C(5)	168.2(6)
C(3)—W—C(5)	98.6(5)	C(4)—W—C(5)	94.8(5)
C(1)—W—C(12)	77.7(5)	C(2)—W—C(12)	94.3(5)
C(3)—W—C(12)	162.5(4)	C(4)—W—C(12)	110.3(5)
C(5)—W—C(12)	74.0(4)	C(1)—W—C(13)	109.8(5)
C(2)—W—C(13)	90.4(5)	C(3)—W—C(13)	163.3(5)
C(4)—W—C(13)	77.8(5)	C(5)—W—C(13)	80.2(4)
C(12)—W—C(13)	32.8(4)	W—C(1)—O(1)	175.0(10)
W—C(2)—O(2)	178.3(13)	W—C(3)—O(3)	179.4(11)
W—C(4)—O(4)	177.7(13)	C(5)—N(1)—C(7)	114.7(13)
C(5)—N(1)—C(8)	127.0(12)	C(7)—N(1)—C(8)	117.2(13)
W—C(5)—N(1)	134.9(9)	W—C(5)—N(2)	117.7(9)
N(1)—C(5)—N(2)	107.4(10)	C(5)—N(2)—C(6)	114.4(12)
C(5)—N(2)—C(11)	120.8(10)	C(6)—N(2)—C(11)	122.6(11)
N(2)—C(6)—C(7)	101.1(11)	N(1)—C(7)—C(6)	101.2(11)
N(1)—C(8)—C(9)	111.0(11)	C(8)—C(9)—C(10)	127.3(15)
N(2)—C(11)—C(12)	110.7(11)	W—C(12)—C(11)	106.7(8)
W—C(12)—C(13)	73.6(9)	C(11)—C(12)—C(13)	121.9(12)
W—C(13)—C(12)	73.6(8)		

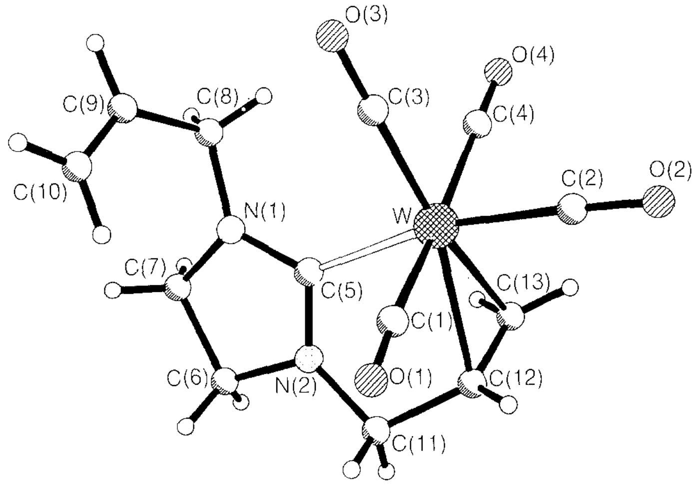


Figure 1. X-ray structure and atom labelling for *(3a)*.

ment to affords *(2)*(11). Hence, *(2)* was always present in the reaction resulting in a modest yield of the metal–carbene products.

Crystallographic analysis of (3a)

The structure of $[(OC)_4W{=}CN(CH_2CH{=}CH_2)\text{-}CH_2CH_2N(CH_2CH{=}CH_2)]$ was confirmed by a single crystal X-ray diffraction investigation (details of which are given in Table 1). Table 2 contains selected bond lengths and bond angles for *(3a)*: Figure 1 shows the main structural features.

Bond angles around C(5) [117.9(8), 107.3(10) and 134.8(9)°] suggest, as previously found(6,7,11), sp^2 character in the carbon atom bonded directly to the metal. Also W—N(1) and W—N(2) atoms are in the same plane.

The W—C(5) bond length [2.21(1) Å] is appropriate for a W-carbene bond(6,7,11). A comparison of the average bond lengths C(5)—N(1,2) in the carbene compound [1.33(2) Å] with the free acetanilide [1.35(3) Å](13) suggests an incipient double bond in the former. The C=C bonds of the two allyl groups reflect the fact that one is bonded to W, whereas the other is free.

Mutually *trans* W—CO bond lengths are significantly longer, by 0.05 Å, than the W—CO *trans* to carbene, in agreement with previous observations than the C carbene is a weaker π-bond acceptor than CO.

The dihedral angle between the five-membered imidazolidin-2-ylidene C(7), N(1), C(5), N(2), C(6) and the plane containing the metal atom and the chelating alkene (containing W, C(12) and C(13) atoms) is 84.8°, indicative of the fact that in the π bonds with the carbene carbon atom and the two alkene carbon atoms, tungsten employs two different and orthogonal t_{2g} orbitals. A similar structure was obtained with molybdenum where the dihedral angle was 94.9°(7).

We have been unable to improve the yield of the carbene compounds, however, the fact that the series is now complete prompts us to report its structural characterization.

Acknowledgement

We thank Federico del Rio for his support in the n.m.r. experiments.

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(Received 5 January 1995) TMC 3427