

Pentacarbonylchromium(0) and -tungsten(0) complexes with the bis(diisopropylamino)cyclopropenylidene ligand [☆]

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Abstract

Bis(diisopropylamino)cyclopropenylidene (**1a**) generated by deprotonation of the cyclopropenylum salt (**5**) with *n*-butyllithium reacts with [(thf)M(CO)₅] (M = Cr, W) to form the carbene complexes [(**1a**)Cr(CO)₅] (**6a**) and [(**1a**)W(CO)₅] (**6b**). The X-ray crystal structure of **6b** is reported. Spectral and structural data of **6a** and **6b** are compared to other [(carbene)M(CO)₅] complexes, confirming **1a** to be a strong donor ligand.

Keywords: Cyclopropenylidene; Carbene; Chromium; Tungsten; Crystal structure

1. Introduction

In 1994 a landmark in lanthanide chemistry was the isolation of the first carbene–lanthanide complexes by Schumann et al. [1] and Arduengo et al. [2]. This development had become possible owing to the availability of stable crystalline imidazol-2-ylidenes [3], which allow observation of the direct reactivity of these nucleophilic carbenes with various reagents in the absence of byproducts from carbene generation.

We are currently studying the synthesis and coordination chemistry of allenylidenes **2** and 2-azaallenylidenes **3** (Fig. 1) [4], which are higher cumulogs of bis(dialkylamino)cyclopropenylidenes **1**. In the course of our studies we became interested in investigating the nucleophilicity and coordination properties of these carbenes in order to gain insight into the ability of the cyclopropenylum system to stabilize ligands of the type **1**, **2** and **3**.

Cyclopropenylidene complexes have been known about for a long time and Öfele, a pioneer in the field of nucleophilic carbenes, reported on the synthesis of pentacarbonyl(diphenylcyclopropenylidene)chromium(0) as early as 1968 [5]. Whereas complexes with the

diphenylcyclopropenylidene are synthesized by the reaction of 3,3-dichlorocyclopropene with metallates [5,6], bis(dialkylamino)cyclopropenylidenes **1** can be used directly for the synthesis of carbene complexes. Yoshida [7] and Weiss [8] have demonstrated that bis(diisopropylamino)cyclopropenylidene (**1a**) can be generated by the reaction of the cyclopropenylum salts **4** or **5** with *n*-butyllithium (Scheme 1). **1a** is stable as a lithium adduct at low temperature and can be used for nucleophilic substitution reactions [7,8]. However, only a few transition metal complexes employing bis(dialkylamino)cyclopropenylidene ligands have been reported [9] and to our knowledge *cis*-PdCl₂[(Me₂NC)₂C](PⁿBu₃) constitutes the only complex characterized by X-ray diffraction [10].

In order to classify the carbene **1a** with regard to other carbenes we chose to study its group VI pentacarbonyl complexes and wish to report on the synthesis and characterization of the bis(diisopropylamino)cyclopropenylidene complexes [(**1**)M(CO)₅] (M = Cr **6a**, W **6b**) along with the X-ray crystal structure of **6b**.

2. Results and discussion

Lithiation of bis(diisopropylamino)cyclopropenylum perchlorate **5** with ⁿBuLi in thf at –78 °C yields a clear solution of the carbene–lithium perchlorate adduct

[☆] This paper is dedicated to Prof. Dr. H. Schumann on the occasion of his 60th birthday.

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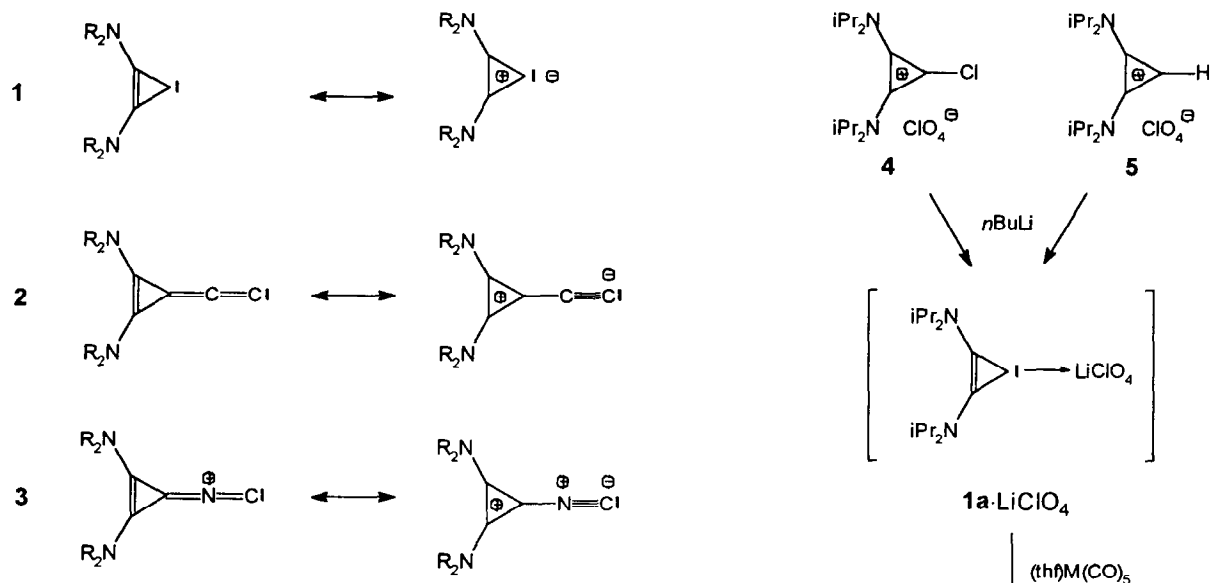


Fig. 1. Cyclopropenylumstabilized carbene **1**, allenylidene **2** and 2-azaallenylidene **3**.

$[(\mathbf{1a})\text{LiClO}_4]$ [9]. Upon addition of photochemically generated $[(\text{thf})\text{M}(\text{CO})_5]$ [11] the carbene complexes **6a/6b** are obtained after chromatographic work-up as yellow, crystalline solids (Scheme 1).

Comparison of the ^{13}C NMR spectra of **6a** and **6b** with the data reported for other $[(\text{carbene})\text{M}(\text{CO})_5]$ complexes **7–10** (Fig. 2, Table 1) allows the classification of the σ -donor/ π -acceptor ratio for bis(diisopropylamino)cyclopropenylidene (**1a**). As expected the carbon atoms of the *trans*-CO groups are significantly deshielded relatively to the equatorial CO ligands. The resonances of the *cis*-carbonyl carbon atoms in **6b** and **7–10** are relatively unaffected by the nature of the carbene ligand, whereas the resonances for the *trans*-carbonyl carbon are obviously a sensitive probe for the σ -donor/ π -acceptor ratio of the *trans*-bonded ligand.

For **10** extensive backbonding to the $\text{C}(\text{C}_6\text{H}_5)_2$ ligand has been discussed [14] and the *trans*-resonance is observed at much lower field (215.3 ppm) compared to **7** (201.2 ppm) where the imidazol-2-ylidene ligand is bonded almost exclusively as a σ -donor [12]. Based on the resonances shown in Table 1 one finds that the

bis(diisopropylamino)cyclopropenylidene (**1a**) represents a nucleophilic carbene with a σ -donor/ π -acceptor ratio which adopts an intermediate position between the imidazol-2-ylidene ligand in **7** and the 1,2-dihydro-benzoxazol-2-ylidene ligand in **8** [13]. The carbene carbon resonances in **6a** (151.1 ppm) and **6b** (136.7 ppm) are found at very high field, documenting the effective stabilization of the carbene carbon, as demonstrated by the mesomeric structures **B** and **C** shown in Fig. 3.

An X-ray crystallographic study of **6b** was undertaken to provide information about the relative contribution of the canonical forms **A–D**. The molecular structure of **6b** is shown in Fig. 4. The tungsten atom is coordinated in a slightly distorted octahedral fashion. A

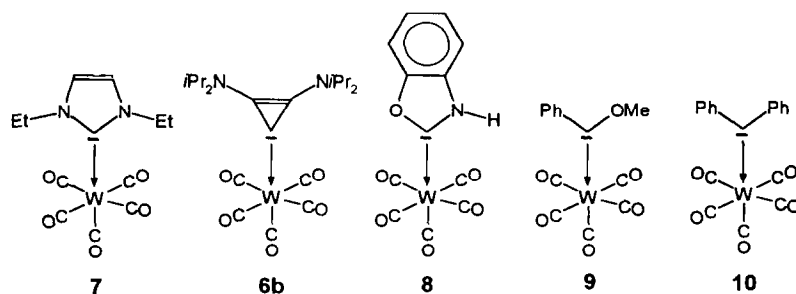


Fig. 2. Selected $[(\text{carbene})\text{W}(\text{CO})_5]$ complexes.

Table 1
Selected ^{13}C NMR chemical shifts (ppm, δ) and bond lengths (\AA)

Compound	C_{trans}	C_{cis}	C_{carbene}	$r(\text{W}-C_{\text{carbene}})$	Lit.
7	201.2	199.0	175.0	2.275(8)	[12]
6b	202.1	198.7	136.7	2.238(7)	
8	202.3	197.8	211.6	2.185(10)	[13]
9	204.6	198.3	323.9	–	[14]
10	215.3	198.4	358.3	2.14(2)	[14]

comparison of the $\text{W}-C_{\text{carbene}}$ distances in **6b**, **7**, **8** and **10** (Table 1) follows the same trend derived from the comparative discussion of the ^{13}C NMR data. The $\text{W}-C_{\text{carbene}}$ distance in **6b** (2.238(5) \AA) is longer than the corresponding distances in **8** (2.185(10) \AA) and **10** (2.14(2) \AA), where the carbene ligands have a lower σ -donor/ π -acceptor ratio. On the other hand imidazol-2-ylidenes show a higher σ -donor/ π -acceptor ratio and consequently one finds an extended $\text{W}-C_{\text{carbene}}$ distance in **7** relatively to **6b**.

The *trans*-effect of the carbene ligand gives rise to a $\text{W}-\text{CO}_{\text{trans}}$ distance which is slightly shortened compared to the $\text{W}-\text{CO}_{\text{cis}}$ bond lengths. Within the 3σ error range the cyclopropenylidene ring exhibits identical C–C bond lengths and internal C–C–C angles of 60° . The distances between the sp^2 hybridized nitrogen atoms and the ring carbon atoms (1.327(6) \AA and 1.335(7) \AA) are significantly shorter than the C–N single bond lengths to the tertiary isopropyl carbon atoms of 1.474(7) \AA on average. These observations clearly demonstrate the contribution of all different mesomeric structures **A–D** depicted in Fig. 3.

3. Conclusions

Cyclopropenylidene **1a** represents a nucleophilic carbene with a high σ -donor/ π -acceptor ratio as shown by comparison of complexes **6a** and **6b** with other [(carbene) $\text{W}(\text{CO})_5$] complexes. The diisopropylamino groups strongly contribute to the stabilization of the carbene center by ($p \rightarrow p$) π bonding from the nitrogen atoms. However, the comparison with complex **7** confirms imidazol-2-ylidenes to be stabilized to a higher degree. Consequently carbenes of the type **1** can only be generated at low temperature and are not isolable at ambient temperature. This will prevent cyclopropenylidene chemistry being as fruitful as the chemistry of

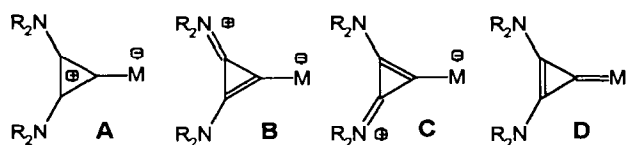


Fig. 3. Mesomeric structures for bis(dialkylamino)cyclopropenylidene complexes.

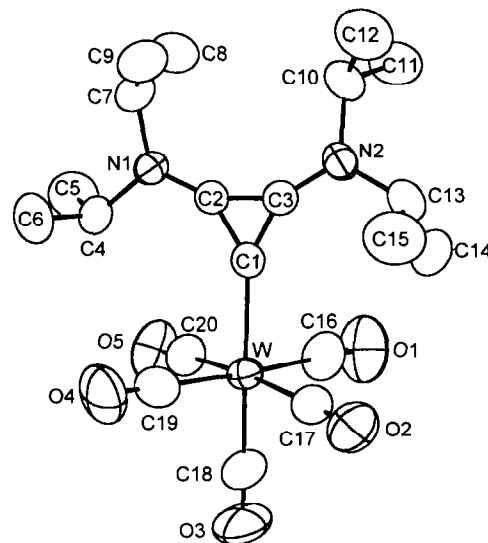


Fig. 4. Molecular structure of **6b**. Selected bond lengths (\AA) and angles ($^\circ$): $\text{W}-\text{C}1$ 2.238(5), $\text{W}-\text{C}16$ 2.021(7), $\text{W}-\text{C}17$ 2.039(6), $\text{W}-\text{C}18$ 1.971(7), $\text{W}-\text{C}19$ 2.019(7), $\text{W}-\text{C}20$ 2.015(7), $\text{C}16-\text{O}1$ 1.135(7), $\text{C}17-\text{O}2$ 1.124(7), $\text{C}18-\text{O}3$ 1.156(7), $\text{C}19-\text{O}4$ 1.153(7), $\text{C}20-\text{O}5$ 1.135(7), $\text{C}1-\text{C}2$ 1.376(7), $\text{C}1-\text{C}3$ 1.373(7), $\text{C}2-\text{C}3$ 1.360(7), $\text{C}2-\text{N}1$ 1.327(6), $\text{C}3-\text{N}2$ 1.335(7), $\text{N}1-\text{C}4$ 1.471(6), $\text{N}1-\text{C}7$ 1.470(6), $\text{N}2-\text{C}10$ 1.481(8), $\text{N}2-\text{C}13$ 1.472(7); $\text{C}1-\text{C}2-\text{C}3$ 60.2(3), $\text{C}2-\text{C}1-\text{C}3$ 59.3(3), $\text{C}1-\text{C}3-\text{C}2$ 60.4(3), $\text{C}2-\text{N}1-\text{C}4$ 117.1(4), $\text{C}2-\text{N}1-\text{C}7$ 123.3(4), $\text{C}3-\text{N}2-\text{C}10$ 121.3(4), $\text{C}3-\text{N}2-\text{C}13$ 120.8(4); maximum deviation of $\text{W}-\text{C}-\text{O}$ and $\text{C}-\text{W}-\text{C}$ angles from 90° or 180° is 4.6.

“Arduengo-carbenes”. On the other hand, owing to the enhanced stability of the cyclopropenylidene system and the ease of substitution reactions in chlorocyclopropenylidene salts **5**, the isolation of free and stable allenylidenes **2** and 2-azaallenylidenes **3** depicted in Fig. 1 is a feasible target, and our results will be presented elsewhere.

4. Experimental section

All operations were performed in an atmosphere of dry argon by using Schlenk and vacuum techniques. Solvents were dried by standard methods and distilled prior to use. NMR spectra were recorded on a Bruker AM 250 (250 MHz) instrument. Infrared spectra were taken on a Perkin-Elmer 983 instrument in KBr. Elemental analyses (C, H, N) were performed at the Freie Universität Berlin on a Heraeus CHN-Rapid elemental analyzer. Mass spectra (EI, 70 eV) were recorded on a Varian MAT 711 instrument. The synthesis of **5** has been reported in the literature [15].

4.1. [Bis(diisopropylamino)cyclopropenylidene]penta-carbonylchromium(0) (**6a**)

A suspension of **5** (1.53 g, 4.5 mmol) in 30 ml of *thf* was treated with *n*-butyllithium (1.8 ml of a 2.5 M

solution in hexane, 4.5 mmol) at -78°C . After stirring for 15 min the clear solution was transferred onto a cooled (-78°C) solution of [(thf)Cr(CO)₅] (photochemically generated from 1 g (4.5 mmol) of Cr(CO)₆ [11]) in 180 ml of thf. After stirring for 30 min at -78°C the reaction mixture was allowed to warm up to room temperature. Stirring was continued for 30 min and the solvents were removed in vacuo. The residue was extracted with dichloromethane and filtered. The crude product was purified chromatographically on Al₂O₃ (4% H₂O) with dichloromethane, giving an air-stable yellow solid. Recrystallization from CH₂Cl₂/Et₂O afforded **6a** as yellow crystals, 623 mg (32%). Anal. Found: C, 55.40; H, 6.57; N, 6.57. C₂₀H₂₈CrN₂O₅ Calc.: C, 56.11; H, 6.59; N, 6.54. ¹H NMR (250 MHz, CDCl₃): δ 1.36 (s br, 24 H, CH₃); 4.22 (s br, 4 H, CH). ¹³C NMR (62.89 MHz, CDCl₃): δ 22.0 (CH₃); 49.7 (CH); 151.1 (C–Cr); 154.3 (N–C); 218.8 (*cis*-CO); 223.0 (*trans*-CO). IR: 2052 (m, CO); 1930 (st, CO); 1907 (st, CO); 1874 (st, C₃) cm⁻¹. MS (70 eV), *m/z* (%): 428 (6) [M⁺]; 316 (11), 288 (100) [LCr(CO)_n⁺] (*n* = 1–0); 52 (7) [Cr⁺].

4.2. [Bis(diisopropylamino)cyclopropenylidene]penta-carbonyltungsten(0) (**6b**)

6b was prepared as described for **6a** from W(CO)₆ (1.0 g, 2.8 mmol), **5** (0.96 g, 2.8 mmol) and *n*-butyllithium (1.2 ml of a 2.5 M solution in hexane, 3.0 mmol). Chromatography on Al₂O₃ (4% H₂O) with dichloromethane and crystallization from CH₂Cl₂/Et₂O afforded **6b** as yellow crystals, 415 mg (26 %). Anal. Found: C, 42.47; H, 5.24; N, 5.11. C₂₀H₂₈N₂O₅W calcd.: C, 42.90; H, 5.04; N, 5.00. ¹H NMR (250 MHz, CDCl₃): δ 1.36 (s br, 24 H, CH₃); 4.20 (s br, 4 H, CH) ppm. ¹³C NMR (62.89 MHz, CDCl₃): δ 21.9 (CH₃); 49.5 (CH); 136.7 (C–W); 151.3 (N–C); 198.7 (*cis*-CO); 202.1 (*trans*-CO) ppm. IR: ν 2059 (m, CO); 1926 (st, CO); 1905 (st, CO); 1872 (st, C₃) cm⁻¹. MS (70 eV), *m/z* (%): 560 (27) [M⁺]; 532 (28), 504 (43), 474 (39), 446 (37), 418 (71) [LW(CO)_n⁺] (*n* = 4–0); 235 (34) [L⁺]; 43 (100) [C₃H₇⁺].

4.3. X-ray crystal structure of **6b** [16]

Air-stable yellow crystals of **6b** were obtained by crystallization from dichloromethane/diethylether (1:1, v/v) at -20°C . Selected crystallographic details: size of crystal 0.25 × 0.35 × 0.45 mm, formula C₂₀H₂₈N₂O₅W, *M* = 560.31 amu, monoclinic, space group *P*2₁/*n* (no. 14), *a* = 12.204(3), *b* = 10.458(2), *c* = 19.256(5) Å, β = 107.17(2)°, *V* = 2348(2) Å³, *Z* = 4, ρ_{exp} = 1.60, ρ_{calc} = 1.585 g cm⁻³, Mo K α radiation (λ = 0.71073 Å, monochromator graphite), μ (Mo K α) = 50.523 cm⁻¹. 2827 symmetry independent diffraction data were measured at 20(2) °C in the 2 θ range

Table 2
Positional and equivalent isotropic thermal parameters for **6b**^a

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} (Å ²)
W	0.37472(2)	0.01785(2)	0.13958(1)	3.562(5)
O1	0.5231(4)	0.1664(6)	0.0565(3)	10.1(1)
O2	0.2012(4)	0.2486(4)	0.1216(2)	7.3(1)
O3	0.5125(5)	0.1505(5)	0.2846(3)	9.9(2)
O4	0.2330(4)	-0.1487(5)	0.2207(2)	7.9(1)
O5	0.5688(3)	-0.1911(4)	0.1806(3)	8.2(1)
N1	0.2544(3)	-0.3164(3)	0.0043(2)	3.29(8)
N2	0.1576(4)	-0.0145(4)	-0.0970(2)	4.0(1)
C1	0.2761(3)	-0.0762(4)	0.0355(2)	3.12(9)
C2	0.2466(3)	-0.1900(4)	-0.0012(2)	2.76(9)
C3	0.2125(4)	-0.0775(4)	-0.0364(2)	3.2(1)
C4	0.3124(4)	-0.3695(4)	0.0766(3)	4.0(1)
C5	0.4091(6)	-0.4588(7)	0.0725(4)	6.8(2)
C6	0.2291(5)	-0.4312(7)	0.1097(3)	6.3(2)
C7	0.1952(4)	-0.4036(5)	-0.0547(3)	4.3(1)
C8	0.2519(5)	-0.4068(6)	-0.1144(3)	5.4(1)
C9	0.0678(5)	-0.3793(6)	-0.0804(3)	5.3(1)
C10	0.1200(4)	-0.0801(5)	-0.1682(3)	4.2(1)
C11	0.1883(6)	-0.0356(7)	-0.2169(3)	6.4(2)
C12	-0.0074(5)	-0.0689(8)	-0.2048(3)	6.4(2)
C13	0.1343(5)	0.1234(5)	-0.0949(3)	5.5(1)
C14	0.2422(6)	0.1988(6)	-0.0665(3)	7.2(2)
C15	0.0501(6)	0.1505(7)	-0.0536(4)	7.9(2)
C16	0.4674(5)	0.1133(6)	0.0850(3)	6.0(2)
C17	0.2600(5)	0.1643(5)	0.1261(3)	4.6(1)
C18	0.4603(6)	0.1022(6)	0.2310(3)	6.3(2)
C19	0.2850(5)	-0.0869(6)	0.1921(3)	5.0(1)
C20	0.4972(4)	-0.1180(6)	0.1629(3)	5.1(1)

^a Estimated standard deviations are given in parentheses. The equivalent isotropic thermal parameter *B*_{eq} is defined as $8/3\pi^2 \times [\sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j]$.

2–45°. Positional parameters for all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were added on calculated positions [*d*(C–H) = 0.95 Å] [17] with *B*_{eq(H)} = 1.3*B*_{eq(C)}. *R* = 2.67, *R*_w = 3.54, GOF = 1.023 for 2583 structure factors *F*_o² ≥ 3 σ (*F*_o²) and 253 refined parameters. Neutral atomic scattering factors [18] were used and all scattering factors were corrected for anomalous dispersion [18]. Positional and equivalent thermal parameters for non-hydrogen atoms are listed in Table 2. A plot of **6b** is presented in Fig. 4.

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