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2-Azaallenylidene complexes: syntheses and structures of chromium and tungsten complexes with a (cyclopropenylidene)-2-azaethenylidene ligand

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Abstract

The reactions of $NEt_4[(CO)_5M(CN)]$ (M = Cr, W) with chloro-bis(diisopropylamino)cyclopropenylium salts $[Cl–C_3(N^iPr)_2]X$, (**1**)X ($X = ClO_4$, OSO_2CF_3), afford cationic 2-azaallenylidene complexes $\{[(CO)_5M=C=N=C_3(N^iPr)_2]^+$ **A** $\leftrightarrow [(CO)_5M–C\equiv N–C_3(N^iPr)_2]^+$ **B**$\}$ (M = Cr, **2a**; M = W, **2b**), in which $C_3(N^iPr)_2$ represents the bis(diisopropylamino)cyclopropenylidene or bis(diisopropylamino)cyclopropenylium moiety, respectively. The IR and NMR spectroscopic characterization of the chromium complexes (**2a**)X ($X = ClO_4$, OSO_2CF_3) and of the tungsten complex (**2b**)$[(CO)_5W(CN)]$ reveals an exceptionally high π-acceptor ability of the 2-azaallenylidene ligand and a high degree of electron delocalization within the metallaheterocumulene system. The X-ray structure determination of (**2b**)$[(CO)_5W(CN)]$ indicates that the structure is best described as a resonance hybrid between two canonical forms, the cumulene form **A** and the isocyanide form **B**. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Heterocumulene; Azaallenylidene; Cyclopropenylium; Chromium; Tungsten

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1. Introduction

Since the discovery of the first allenylidene complexes in 1976 by E.O. Fischer [1] and H. Berke et al. [2], considerable efforts have been devoted to exploring the chemistry of metallacumulenes $[M(=C)_n=CR_2]$ during the last 25 years. In particular, allenylidene complexes ($n = 2$), which are higher cumologs of alkylidene ($n = 0$) [3] and vinylidene complexes ($n = 1$) [4], have become a well established and thoroughly studied class of organometallic compounds [5]. This development had been very much stimulated by Selegue in 1982, who first demonstrated that allenylidenes are easily formed by the activation of 2-propyn-1-ols at electron-rich metal centers via spontaneous dehydration of intermediate hydroxymethylvinylidene ligands [6]. In addition, significant progress has been made in further increasing the length of these cumulative molecular wires, and thus stable complexes containing highly unsaturated butatrienylidene ($n = 3$) [7] and pentatetraenylidene ligands ($n = 4$) [8] have been isolated in recent years.

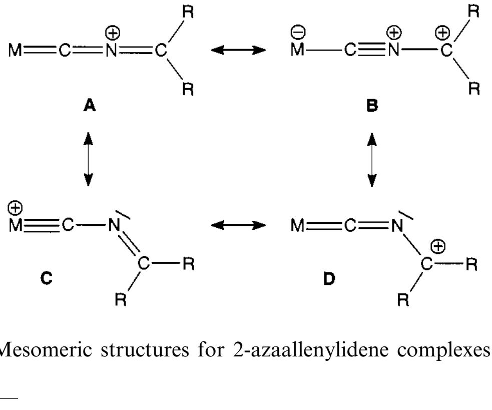

Fig. 1. Mesomeric structures for 2-azaallenylidene complexes.

In contrast, complexes containing unsaturated heterocumulenylidene ligands bound in an end-on fashion are still rare [5a] with the most prominent examples

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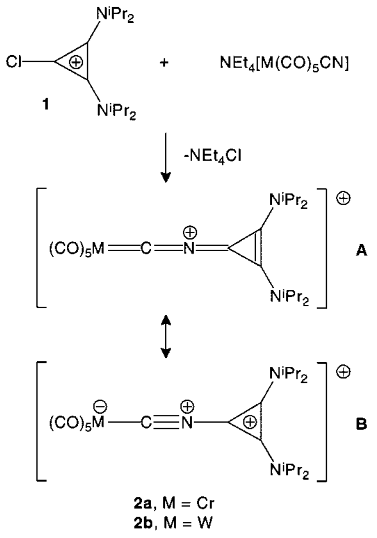

Scheme 1.

being 2-azaallenylidene complexes, [M=C=N=CR$_2$]$^+$, which are formally derived from allenylidene complexes [M=C=C=CR$_2$] by isoelectronic substitution of the central carbon atom by N$^+$ [9,10]. The bonding in the M–C–N–C–unit can tentatively be described by varying contributions from the mesomeric structures **A**–**D** (Fig. 1), and H. Fischer et al. have demonstrated that the relative electron distribution in these systems strongly depends on the nature of the residues R and on the electron release ability of the metal center M. Linear [9] (canonical forms **A** and **B**) as well as substantially bent derivatives [10] (canonical forms **C** and **D**) have been described.

In the course of our work on transition metal complexes with dipolar cycloheptatrienyl ligands [11], we have demonstrated that mono- and bimetallic allenylidene complexes [M=C=C=CR$_2$] containing (cycloheptatrienylidene)ethenylidene ligands [12] exhibit strong dipolar characteristics due to the well known ability of the tropylium system to effectively stabilize a positive charge, thus leading to a significant contribution from the dipolar canonical form [M$^-$–C≡C–CR$_2^+$]. In continuation, we have also been interested in employing related systems containing cyclopropenylidene or cyclopropenylium groups [13], respectively, which should also result in the formation of significantly polarized compounds. Whereas our attempts to prepare the corresponding allenylidene complexes are still under investigation, we report herein on the syntheses and characterization of new cationic 2-azaallenylidene complexes {[(CO)$_5$M=C=N=C$_3$(N^{i}Pr)$_2$]$^+$↔[(CO)$_5$M–C≡N–C$_3$(N^{i}Pr)$_2$]$^+$} (M = Cr, **2a**; M = W, **2b**), in which C$_3$(N^{i}Pr)$_2$ represents the bis(diisopropylamino)cyclopropenylidene or bis(diisopropylamino)cyclopropenylium moiety, respectively.

2. Results and discussion

Two routes are conceivable for the synthesis of 2-azaallenylidene complexes: (a) abstraction of an alkoxide from the metal-bound carbon of 2-azaallenyl complexes [M=C(OR)N=CR$_2$] and (b) abstraction of a leaving group X from the isocyanide α-carbon atom of isocyanide complexes [M(CNCXR$_2$)]. To our knowledge, the latter reaction has been employed only once in the preparation of a very reactive, cationic dichloro-2-azaallenylidene complex by chloride abstraction from trichloromethyl isocyanide in [(CO)$_5$Cr(CNCCl$_3$)] [9b]. In principle, it is this method, which is used here for the synthesis of the cationic complexes [(CO)$_5$M=C=N=C$_3$(N^{i}Pr)$_2$]$^+$ (M = Cr, **2a**; M = W, **2b**). Hence, the reaction of the cyano complex NEt$_4$[(CO)$_5$Cr(CN)] with chloro-bis(diisopropylamino)cyclopropenylium perchlorate or triflate results in the formation of the chromium complexes (**2a**)X (X = ClO$_4$, OSO$_2$CF$_3$), presumably via nucleophilic attack of the cyano nitrogen atom at the cyclopropenylium system followed by elimination of a chloride anion (Scheme 1). In a similar way, Weiss et al. directly obtained dicationic phosphoniocyclopropenylium derivatives on reaction of phosphines with chlorocyclopropenylium salts [14].

In contrast to other 2-azaallenylidene complexes [9], both compounds containing **2a** are perfectly airstable and can be obtained as colorless crystals after recrystallization from dichloromethane–diethyl ether. The counterion does not affect the spectroscopic properties of the cation **2a**, and the IR spectra of both salts exhibit three CO absorptions (2127, 2053, 1953 cm^{-1}) as expected for a complex with local C_{4v} symmetry at the metal center. In addition, a very strong absorption band is observed at 1894 cm^{-1}, which can be assigned to the asymmetric stretching mode of the CNC moiety in analogy to the values measured for related systems. For example, [(CO)$_5$Cr=C=N=CPh$_2$]BF$_4$, (**3a**)BF$_4$ (Fig. 2), shows CO absorptions at 2103, 2031, 2008 cm^{-1} together with $\tilde{\nu}$(CNC) at 1888 cm^{-1} [9b]. These observations indicate that complex **2a** can be regarded as a 2-azaallenylidene complex with an essentially linear C–N–C arrangement as expressed by a resonance hybrid between the canonical forms **A** and **B** shown in Fig. 1 and Scheme 1, respectively. It should be noted, however, that an unambiguous assignment of the vibrational bands in these complexes does not always appear to be feasible due to various possible couplings between the different stretching modes. Therefore, we refrain from further comparison of these data with other systems such as isocyanide complexes as this might lead to severe misconclusions.

In our hands, ^{13}C-NMR spectroscopy seems to be a better probe for the comparative σ-donor/π-acceptor abilities of the ligands in various [(CO)$_5$M(CNR)] com-

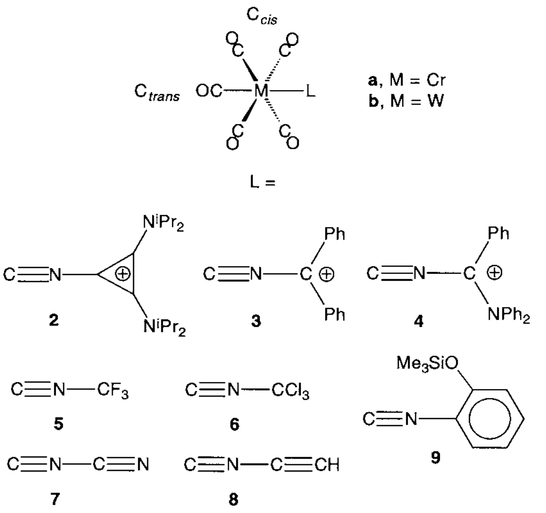

Fig. 2. Selected 2-azaallenylidene and isocyanide complexes.

plexes (Fig. 2), and Table 1 summarizes selected ^{13}C-NMR resonances of chromium complexes **2a**–**9a** and tungsten complexes **2b**–**5b** and **9b**. Again comparison with **3a** supports the conclusion that the ligand in **2a** is indeed best regarded as a 2-azaallenylidene ligand. Hence, the C_α carbon resonance is observed at 195.7 ppm only slightly downfield from the value found for **3a** (200.4 ppm). In contrast, the corresponding resonances in typical alkyl [15] or aryl isocyanide complexes [16] are observed at significantly lower field, e. g. at 173.0 ppm in **9a**, in which the isocyanide nitrogen atom is also attached to a sp^2 carbon atom [17].

Furthermore, the chemical shifts for the carbonyls in **2a** also compare well with the values obtained for chromium complexes of particularly electron-deficient isocyanides [18–21], such as ethynyl, trichloromethyl and cyano isocyanide (Table 1). Thus, the ligand in **2a** proves to be among the strongest π-acceptors, as the presence of such ligands does usually cause a significant shielding of the carbonyl groups, which are competing for π-back-donation from the metal center. In addition, the *trans* influence of the ligand on the carbonyl groups is decreased, and the difference $\Delta\delta$ between the *trans* and *cis* ^{13}CO resonances vanishes [22]. In case of very strong π-acids this value might become zero or even negative (Table 1).

The preparation of tungsten complexes containing the cation **2b** proved to be slightly more complex than anticipated. Heating a mixture of $NEt_4[(CO)_5W(CN)]$ with chloro-bis(diisopropylamino)cyclopropenylium perchlorate overnight did not lead to completion. Instead, yellow crystals were isolated from the reaction mixture in less than 50% yield based on $[ClC_3(N^iPr)_2]ClO_4$. The IR spectrum exhibits a very strong $\tilde{\nu}(CNC)$ absorption at 1877 cm^{-1} clearly revealing the formation of a 2-azaallenylidene complex. In addition, several CO stretching frequencies are observed together with a band at about 2100 cm^{-1} indicative of the presence of the anion $[(CO)_5W(CN)]^-$ in the crystalline product [28]. The ^{13}C-NMR spectrum displays two sets of *cis* and *trans* carbonyl resonances in a 1:1 ratio as well as resonances at 177.2 and 137.2 ppm, which can be assigned to the $WC_\alpha N$ carbon atoms in

Table 1
Selected ^{13}C-NMR data of chromium complexes **2a–9a** and tungsten complexes **2b–5b**, **9b** [a]

$[(CO)_5M(CNR)]$	CO_{trans}	CO_{cis}	$\Delta\delta$ [b]	$MC_\alpha N$	Reference
^{13}C chemical shifts (ppm/Me_4Si)					
2a, $R{=}C_3(N^iPr)_2^+$	212.8	212.4	0.4	195.7	
3a, $R{=}CPh_2^+$	211.8	209.5	2.3	200.4	[9b]
4a, $R{=}C(NPh_2)Ph^+$	215.2	210.9	4.3	211.2	[9d]
5a, CF_3	211.5	211.7	−0.2	211.1	[18b]
6a, CCl_3	213.5	212.6	0.9	200.7	[19b]
7a, CN	212.6	212.6	0	200.0	[20]
8a, CCH	213.6	213.6	0	174.2	[21]
9a, $R{=}C_6H_4$-2-$OSiMe_3$	216.9	214.6	2.3	173.0	[17]
^{13}C chemical shifts (ppm/Me_4Si)					
2b, $R{=}C_3(N^iPr)_2^+$	192.8	192.3	0.5	177.2	
Anion in (**2b**)$[(CO)_5W(CN)]$	200.9	197.8	3.1	137.2	
3b, $R{=}CPh_2^+$	191.7	189.1	2.6	182.3	[9b]
4b, $R{=}C(NPh_2)Ph^+$	196.1	191.1	5.0	191.7	[9d]
5b, CF_3	191.3	191.9	−0.6	188.9	[18b]
9b, $R{=}C_6H_4$-2-$OSiMe_3$	196.5	194.1	1.4	153.6	[16c]
^{13}C–^{183}W coupling constants (Hz)					
2b, $R{=}C_3(N^iPr)_2^+$	121	126		131	
Anion in (**2b**)$[(CO)_5W(CN)]$	140	125		92	

[a] All spectra were recorded in CCl_4, $CDCl_3$ or CD_2Cl_2.
[b] $\Delta\delta = \delta(CO_{trans})$–$\delta(CO_{cis})$.

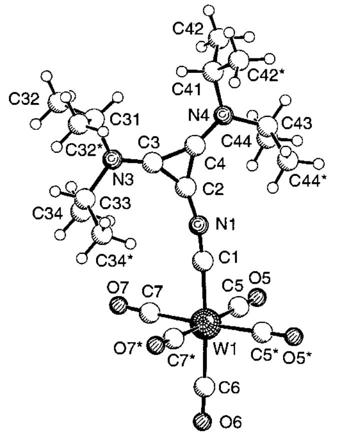

Fig. 3. Molecular structure of the cation in (**2b**)[$(CO)_5W(CN)$]. Selected bond lengths (Å) and angles (°): W1–C1 2.054(6), W1–C5 2.038(6), W1–C6 2.044(8), W1–C7 2.031(6), C1–N1 1.183(7), N1–C2 1.338(7), C2–C3 1.371(8), C2–C4 1.363(7), C3–C4 1.432(8), C3–N3 1.296(8), C4–N4 1.296(7); W1–C1–N1 175.9(5), C1–N1–C2 168.5(6).

the cation **2b** and in the anion [$(CO)_5W(CN)$]$^-$, respectively. Consequently, it can be concluded that crystals of the composition (**2b**)[$(CO)_5W(CN)$] must have formed. Variation of the metal center (**2a** → **2b**) induces a diamagnetic shift to higher field of all metal-bound carbon resonances. Comparison of the NMR data of **2b** to those of related tungsten complexes (Table 1) confirms the conclusions drawn for the chromium derivatives (vide supra).

In addition, the NMR spectroscopic characterization of (**2b**)[$(CO)_5W(CN)$] allows the direct comparison of the properties of the 2-azaallenylidene ligand in the cation and of the cyanide ligand in the anion. As expected, the presence of the weaker π-acceptor, the cyanide, results in deshielding of the carbonyl groups and in a larger difference $\Delta\delta$ between the chemical shifts of *cis* and *trans* ^{13}CO. Furthermore, one can compare the ^{13}C–^{183}W coupling constants (Table 1), which are a measure of metal–ligand σ-bonding [22]. In agreement with the synergistic model for metal–carbon bonding, the σ-bond is strengthened, indicated by an increase in $J(^{13}C–^{183}W)$, as increased π-bonding occurs [22]. Consequently, the 2-azaallenylidene ligand exhibits a much larger value of $J(^{13}C–^{183}W)$ than the cyanide. Simultaneously, the coupling constant for the *trans* carbonyl group decreases, whereas the coupling to the *cis* carbonyl carbon atoms remains almost completely unaffected.

An X-ray crystallographic study was undertaken to unambiguously prove the formation of (**2b**)[$(CO)_5W(CN)$] and to provide information about the relative contribution of the various canonical forms describing complexes of type **2**. The molecular structure of the cation **2b** is shown in Fig. 3. The cation lies on a crystallographic mirror plane including the $CNC_3(NC_2)_2$ fragment of the ligand, the metal center and the *trans* CO group. The tungsten atom is coordinated in an almost perfectly octahedral fashion. Although the C–N–C unit deviates from linearity, the ligand in **2b** can still be regarded as being essentially linear, with angles at N1 and C1 168.5(6) and 175.9(5)°, respectively. Similar deviations from perfectly linear structures have been observed for structurally characterized 2-azaallenylidene complexes [$(CO)_5Cr{=}C{=}N{=}C(C_6H_4)_2$-O]$BF_4$ (**10**) [9a,b] and [$Cp(CO)(PR_3)Mn{=}C{=}N{=}CPh_2$]-$BF_4$ (**11**) (R = *o*-tolyl) [9c] as well as for several allenylidene complexes of the type [$(CO)_5M{=}C{=}C{=}CR_2$] [[8c],[23]]. Both carbon–nitrogen distances differ significantly (C1–N1 = 1.183(7) versus N1–C2 = 1.338(7) Å), which is in good agreement with the bond lengths in **10** and **11** (1.184(7), 1.343(7) and 1.184(9), 1.313(9) Å). This reveals that in the solid state the bonding within the M–C–N–C moiety is best described by canonical form **B** with only little contribution from the cumulene form **A**. Nevertheless, structure determinations of alkyl and aryl isocyanide pentacarbonyltungsten complexes reveal longer W–C and significantly shorter C–N distances due to the decreased π-accepting abilities of these ligands [15b,16a,22,24]. The same holds true for dialkylamino-substituted allenylidene complexes of tungsten [8c], in which the W–C_α distance to the attached ligand is substantially increased in comparison to **2b** (W–C1 = 2.031(6) Å). Furthermore, all W–C and C–O distances in **2b** are identical within experimental error indicating that the $CNC_3(N^iPr)_2^+$ ligand almost acts as a sixth carbonyl ligand.

Finally, it is noteworthy to discuss the structural parameters of the cyclopropenylidene residue. Very short distances between the ring carbon atoms and the sp^2 hybridized nitrogen atoms are observed together with unequivalent intra-ring C–C bond lengths, which shows that the positive charge on the cyclopropenyl ring is effectively stabilized by $(p–p)_\pi$ donation from the nitrogen atoms. Please note, that several additional mesomeric structures must be considered to describe this charge delocalization within the bis(diisopropylamino)cyclopropenylidene or -cyclopropenylium residue, respectively [13a,25]. In view of this very strong π-donation from the diisopropylamino groups, the strong overall electron-withdrawing ability of the ligand in complexes **2** appears to be somewhat surprising. This indicates, however, that a discussion of the bonding in these systems cannot only be assessed by an oversimplified comparison of relative ligand π-acidities and that σ-effects must also be taken into account (vide supra) [22].

To complete this contribution, the molecular structure of the anion in (**2b**)[$(CO)_5W(CN)$] is depicted in Fig. 4. We are unaware of any X-ray crystallographic study of salts containing isolated [$(CO)_5M(CN)$]$^-$ anions with M = Cr, Mo or W, although these systems

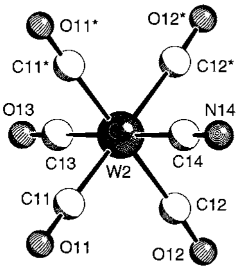

Fig. 4. Molecular structure of the anion in (**2b**)[(CO)$_5$W(CN)]. Bond lengths (Å): W2–C11 2.006(5), W2–C12 2.088(6), W2–C13 2.050(8), W2–C14 2.028(9), C11–O11 1.142(6), C12–O12 1.163(7), C13–O13 1.117(9), C14–N14 1.120(10).

have been widely used as ligands for the complexation of other transition metals, in the formation of hydrogen bridged species and in template synthesis of various isocyanides [19a]. Similar to the cation (vide supra) the anion lies on a crystallographic mirror plane bisecting the plane including C11, C11*, C12 and C12*. Therefore, we tentatively rule out the possibility that the cyanide nitrogen atom is attached to one of these carbon atoms and assume that it must be localized on the O–C–W–C–N axis, which is included in the crystallographic mirror plane. Attaching the nitrogen atom to C14 results in a favourable R value compared to linking it to C13. Disorder of the nitrogen and oxygen atoms, however, can not be excluded with absolute certainty, thus preventing a detailed discussion of the bonding geometry.

In summary, we have presented a new method for the preparation of chromium and tungsten 2-azaallenylidene complexes with a bis(diisopropylamino)cyclopropenylidene residue. Although this moiety is able to effectively stabilize a positive charge the ligand still behaves like a ‘true’ 2-azaallenylidene ligand rather than like a conventional isocyanide ligand. Due to this behavior and due to the tremendously enhanced stability of these species, the synthesis of related allenylidene and higher cumulenylidene complexes and even the isolation of free 2-azaallenylidenes and allenylidenes seem to be feasible goals, in particular in view of the possibility to generate the related nucleophilic carbenes, the bis(dialkylamino)cyclopropenylidenes [13,25], and in view of reports on the preparation of stable diazoniumcyclopropenylium [26] and alkynylcyclopropenylium salts [27].

3. Experimental

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. $NEt_4[(CO)_5Cr(CN)]$, $NEt_4[(CO)_5W(CN)]$ [28] and the chloro-bis(diisopropylamino)cyclopropenylium salts, (**1**)ClO_4 and (**1**)OSO_2CF_3, [29] were prepared according to published procedures.

3.1. *{[Bis(diisopropylamino)cyclopropenylidene]-2-azaethenylidene}-pentacarbonylchromium(0)-perchlorate, (**2a**)ClO$_4$*

A solution of (**1**)ClO_4 (746 mg, 2.0 mmol) and $NEt_4[(CO)_5Cr(CN)]$ (700 mg, 2.0 mmol) in CH_2Cl_2 (50 ml) was heated under reflux overnight. The yellow reaction mixture was allowed to cool to room temperature, and water (20 ml) was added. The organic phase was washed twice with water (30 ml) and then dried over Na_2SO_4. After evaporation of the solvent, the brown residue was recrystallized from CH_2Cl_2–diethyl ether at -20°C to afford colorless, airstable crystals. Yield: 550 mg (53%). Anal. Found: C, 45.04; H, 5.06; N, 7.36. $C_{21}H_{28}N_3O_9ClCr$, Calc.: C, 45.54; H, 5.10; N, 7.59%. ^{1}H-NMR ($CDCl_3$, 250 MHz): δ 4.10 (m, 2H, CH), 3.90 (m, 2H, CH); 1.50 (d, 24H, CH_3) ppm. ^{13}C-NMR ($CDCl_3$, 62.90 MHz): δ 212.8 (CO_{trans}); 212.4 (CO_{cis}); 195.7 (WCN); 124.3 (C=C); 90.1 (WCNC); 58.2 (CH); 48.6 (CH); 22.4 (CH$_3$); 20.7 (CH$_3$) ppm. IR (CH_2Cl_2): $\tilde{\nu}$ 2127 (m, CO); 2053 (st, CO); 1953 (st, CO); 1894 (st, C=N=C) cm^{-1}. MS (FAB, positive ions): m/z (%) 454 (60) [M$^+$] and peaks for $[LCr(CO)_n]^+$ ($n = 4-0$).

3.2. *{[Bis(diisopropylamino)cyclopropenylidene]-2-azaethenylidene}-pentacarbonylchromium(0)-trifluoromethanesulfonate, (**2a**)OSO$_2$CF$_3$*

Complex (**2a**)OSO_2CF_3 was prepared following the same procedure as described in Section 3.1 Hence, colorless, airstable crystals were obtained from the reaction of (**1**)OSO_2CF_3 (1.21 g, 2.9 mmol) with $NEt_4[(CO)_5Cr(CN)]$ (1.0 g, 2.9 mmol) in CH_2Cl_2 (50 ml). Yield: 1.12 g (65%). Anal. Found: C, 43.92; H, 4.68; N, 7.05. $C_{21}H_{28}N_3O_8F_3SCr$, Calc.: C, 43.78; H, 4.87; N, 6.96%. MS (FAB, positive ions): m/z (%) 454 (63) [M$^+$] and peaks for $[LCr(CO)_n]^+$ ($n = 4$-0). The IR and NMR spectroscopic data obtained for the cation in (**2a**)OSO_2CF_3 are identical to those described for the cation in (**2a**)ClO_4 (see Section 3.1).

3.3. *{[Bis(diisopropylamino)cyclopropenylidene]-2-azaethenylidene}-pentacarbonyltungsten(0)-pentacarbonyltungstate, (**2b**)[(CO)$_5$W(CN)]*

A solution of (**1**)ClO_4 (2.34 g, 6.3 mmol) and $NEt_4[(CO)_5W(CN)]$ (3.03 g, 6.3 mmol) in CH_2Cl_2 (80 ml) was heated under reflux overnight. The yellow–brown reaction mixture was allowed to cool to room temperature, and water (50 ml) was added. The organic phase was washed twice with water (50 ml) and then dried over Na_2SO_4. After evaporation of the solvent, the dark brown residue was recrystallized from CH_2Cl_2–diethyl ether at -20°C to afford yellow, airstable crystals. Yield: 1.87 g (63% based on $NEt_4[(CO)_5W(CN)]$, 32% based on (**1**) ClO_4). Anal. Found: C, 34.33; H, 3.07; N, 5.96. $C_{27}H_{28}N_4O_{10}W_2$, Calc.: C, 34.64; H, 3.01; N, 5.98%. ^{1}H-NMR (CD_2Cl_2, 200 MHz): δ 4.06 (m, 2H, C*H*); 3.91 (m, 2H, C*H*); 1.44 (d, 12H, CH_3); 1.40 (d, 12H, CH_3) ppm. ^{13}C-NMR (CD_2Cl_2, 50.33 MHz): δ 200.9 (anion, CO_{trans}, $^1J(^{13}C–^{183}W) = 140$ Hz); 197.8 (anion, CO_{cis}, $^1J(^{13}C–^{183}W) = 125$ Hz); 192.8 (cation, CO_{trans}, $^1J(^{13}C–^{183}W) = 121$ Hz); 192.3 (cation, CO_{cis}, $^1J(^{13}C–^{183}W) = 126$ Hz); 177.2 (cation, W*C*N, $^1J(^{13}C–^{183}W) = 131$ Hz); 137.2 (anion, W*C*N, $^1J(^{13}C–^{183}W) = 92$ Hz); 124.6 (*C*=*C*); 90.3 (WCN*C*); 58.4 (*C*H); 49.0 (*C*H); 22.3 (CH_3); 20.6 (CH_3) ppm. IR (CH_2Cl_2): $\tilde{\nu}$ (w, CN); 2058 (m, CO); 2020 (sh, CO); 1973 (st, CO); 1920 (st, CO); 1877 (st, CNC) cm^{-1}.

3.4. X-ray crystal structure of (2b)[(CO)$_5$W(CN)] [30]

Yellow crystals were obtained by crystallization from dichloromethane–diethyl ether at -20°C. Selected crystallographic details: crystal size 0.20 × 0.20 × 0.20 mm, formula $C_{21}H_{28}N_3O_5W \cdot C_6NO_5W$, $M = 936.23$, $a = 26.527(1)$, $b = 10.596(1)$, $c = 12.410(1)$ Å, $V = 3488.2(5)$ Å^3, $\rho_{calc} = 1.783$ g cm^{-3}, $\mu = 66.43$ cm^{-1}, empirical absorption correction via SORTAV ($0.350 \leq T \leq 0.350$), $Z = 4$, orthorhombic, space group *Pnma* (No. 62), $\lambda = 0.71073$ Å, $T = 198$ K, ω and π scans, 8321 reflections collected ($\pm h, \pm k, \pm l$), $[(\sin\theta)/\lambda] = 0.67$ Å^{-1}, 4542 independent ($R_{int} = 0.034$) and 3219 observed reflections $[I \geq 2\sigma(I)]$, 227 refined parameters, $R = 0.036$, $wR^2 = 0.083$, maximum residual electron density 0.86 (-1.44) e Å^{-3} close to tungsten, hydrogens calculated and refined as riding atoms. Data set was collected with Nonius–KappaCCD diffractometer, equipped with a rotating anode generator Nonius FR591. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN [30], absorption correction SORTAV [31], structure solution SHELXS-97 [32], structure refinement SHELXL-97 [33], graphics SCHAKAL [34].

4. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 148824. Copies of the data can be obtained free of charge on application to: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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