

Metal–carbon multiple bonds: [2 + 2] cycloaddition of nitrilium salts across a metal–carbon triple bond; synthesis and structure of iminocarbene complexes of tungsten [☆]

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Abstract

The aminocarbyne complex $\text{Cp}^*(\text{CO})_2\text{W}\equiv\text{CNEt}_2$ ($\text{Cp}^* = \text{C}_5\text{Me}_5$) (**1**) undergoes a selective [2 + 2] cycloaddition reaction with the nitrilium salt $[\text{MeC}\equiv\text{NMe}]\text{BF}_4$ to afford the iminocarbene complex $[\text{Cp}^*(\text{CO})_2\text{W}\{=\text{C}(\text{NEt}_2)\text{C}(\text{Me})=\text{NMe}\}]\text{BF}_4$ (**2**). Alternatively, the analogous iminocarbene complexes $[\text{Cp}^*(\text{CO})_2\text{W}\{=\text{C}(\text{NMe}_2)\text{C}(\text{Me})=\text{NEt}\}]\text{BF}_4$ (**5**: M = Mo; **6**: M = W) can be obtained by methylation of the η^2 -1,4-diaza-3-methylbutadien-2-yl complexes $\text{Cp}^*(\text{CO})_2\text{M}[\text{C}(\text{NMe})\text{C}(\text{Me})\text{NEt}]$ (**3**: M = Mo; **4**: M = W) with $[\text{Me}_3\text{O}]\text{BF}_4$. The solid-state structure of **2** suggests the presence of an η^3 -bonded iminocarbene ligand and reveals a close electronic relationship between **2**, **5** and **6** and Mo^{II} or W^{II} η^3 -vinylcarbene complexes.

Keywords: Cycloaddition; Carbyne complexes; Iminocarbene complexes; Nitrilium salts; C–C coupling

1. Introduction

On the basis of the isolobal relationship between a carbyne ligand CR and a $\text{CpM}(\text{CO})_2$ fragment (M = Cr, Mo, or W) [1], transition-metal carbyne complexes of the type $(\eta^5\text{-C}_5\text{R}'_5)(\text{CO})_2\text{M}\equiv\text{CR}$ ($\text{R}' = \text{H}$ or Me; R = alkyl, aryl, amino) [2] can be regarded as organometallic analogues of the alkynes [3]. This analogy is reflected in the reactions of these compounds. For example, the carbyne complex $\text{Cp}(\text{CO})_2\text{W}\equiv\text{CTol}$ ($\text{Cp} = \text{C}_5\text{H}_5$; Tol = $\text{C}_6\text{H}_4\text{Me-4}$) shows similar reactivity to that of alkynes, adding a variety of 14e or 16e metal fragments to the metal–carbon triple bond to give heterodinuclear metal complexes which contain a double-bridging carbyne ligand [4]. Similarly, the carbyne complexes $(\eta^5\text{-C}_5\text{R}'_5)(\text{CO})_2\text{W}\equiv\text{CTol}$ ($\text{R}' = \text{H}$, Me) behave like alkynes and react with a variety of homodinuclear metal complexes such as $\text{Co}_2(\text{CO})_8$ or $\text{Cp}_2\text{Mo}_2(\text{CO})_4$, to give trimetallic clusters containing a μ_3 -carbyne ligand [2c,5]. Moreover, the carbyne complexes $\text{Cp}(\text{CO})_2\text{M}\equiv$

CR (M = Mo, W; R = Ph, Tol) like alkynes undergo [3 + 2] cycloaddition reactions with organic azides to afford 1-metalla-2,3,4-triazole complexes [6,7].

In comparison, [2 + 2] cycloadditions of the carbyne complexes $(\eta^5\text{-C}_5\text{R}'_5)(\text{CO})_2\text{M}\equiv\text{CR}$ have not yet been reported, although analogous reactions of alkynes are well known [8]. In general, [2 + 2] cycloaddition reactions of Fischer-type carbyne complexes are rare, including the reaction of $[\text{NEt}_4][(\text{CO})_4\text{Mo}(\mu\text{-PPh}_2)_2\text{W}(\text{CO})_2\text{CNEt}_2]$ with CO_2 [9] or the reactions of $[\text{Cp}(\text{CO})_2\text{Re}\equiv\text{CTol}][\text{BX}_4]$ (X = Cl, Ph) with imines, nitroso and azo compounds [10]. In the present work we report the synthesis and structure of iminocarbene complexes taking advantage of (a) the facile [2 + 2] cycloaddition reaction of $\text{Cp}^*(\text{CO})_2\text{W}\equiv\text{CNEt}_2$ (**1**) with a nitrilium salt and (b) the selective methylation of the η^2 -1,4-diaza-3-methylbutadien-2-yl complexes $\text{Cp}^*(\text{CO})_2\text{M}[\text{C}(\text{NMe})\text{C}(\text{Me})\text{NEt}]$ (**3**: M = Mo; **4**: M = W) with $[\text{Me}_3\text{O}]\text{BF}_4$.

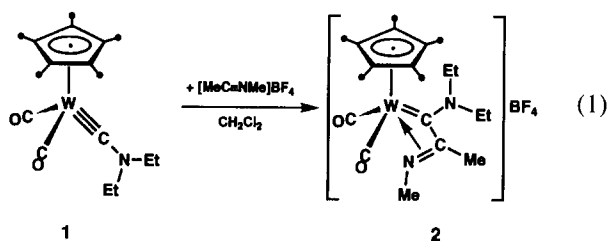
2. Results and discussion

When a solution of the aminocarbyne complex **1** [11] in CH_2Cl_2 was treated with 1 equiv. of $[\text{MeC}\equiv\text{NMe}]\text{BF}_4$

[☆] Dedicated to Professor Dr. H. Brunner on the occasion of his 60th birthday.

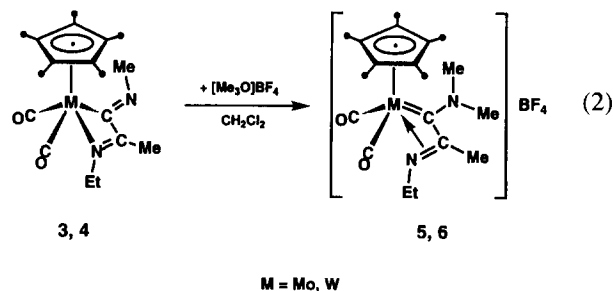
* Corresponding author.

at ambient temperature, a fast and selective C–C coupling reaction occurred, which was accompanied by a colour change from yellow to red and resulted in the formation of the iminocarbene complex **2** [Eq. (1)].



Evidence for the clean conversion of **1** to **2** was provided by the IR spectrum of the reaction solution, which revealed that the two $\nu(\text{CO})$ absorptions of the starting material at 1930 and 1841 cm^{-1} had been replaced at the end of the reaction by the two $\nu(\text{CO})$ absorptions of the product at 1986 and 1926 cm^{-1} . Complex **2** was isolated as a red–brown solid in 72% yield after evaporation of the solvent and recrystallization of the residue from THF/ Et_2O /*n*-pentane. It is soluble in MeCN, CH_2Cl_2 and THF, but insoluble in Et_2O and *n*-pentane, and decomposes at 131°C when heated in a sealed capillary under nitrogen.

Alternatively, iminocarbene complexes like **2** were formed when the η^2 -1,4-diaza-3-methylbutadien-2-yl complexes $\text{Cp}^*(\text{CO})_2\text{M}[\text{C}(\text{NMe})\text{C}(\text{Me})\text{NEt}]$ (**3**: M = Mo; **4**: M = W) [12] were treated with slightly less than 1 equiv. of $[\text{Me}_3\text{O}]\text{BF}_4$ [Eq. (2)]. Again IR monitoring of these reactions revealed a clean conversion of the starting materials to the products **5** and **6**, which were isolated as red–brown solids that are soluble in CH_2Cl_2 and THF and melt without decomposition at 66°C and 64°C, respectively.



Two strong $\nu(\text{CO})$ absorptions of almost equal intensity are observed in the IR spectra of the iminocarbene complexes **2**, **5** and **6** indicating the presence of two *cis*-oriented carbonyl ligands. In addition, complexes **2**,

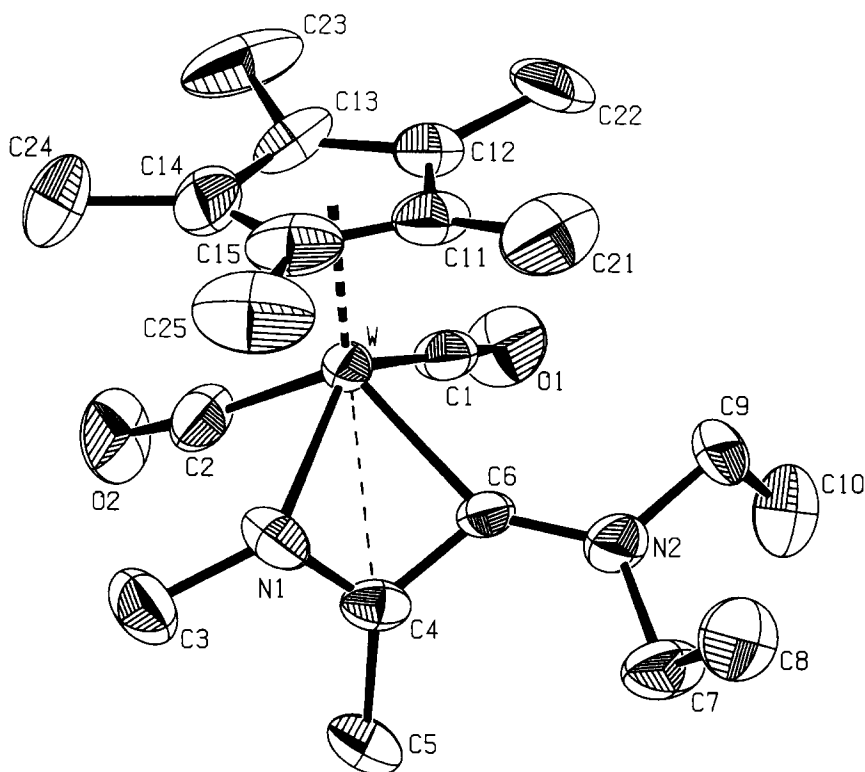


Fig. 1. ORTEP plot of the cation in **2** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (pm) and bond angles ($^\circ$) with estimated standard deviations are: W–N1, 220.6(3); W–C1, 198.0(4); W–C2, 199.6(4); W...C4, 245.4(3); W–C6, 206.5(3); W–Cp*, 199; N1–C4, 131.8(4); N2–C6, 132.1(3); C4–C6, 141.8(4); N1–W–C1, 133.3(1); N1–W–C2, 86.5(1); N1–W–C6, 62.7(1); N1–W–Cp*, 113; C1–W–C2, 79.4(1); C1–W–C6, 84.7(1); C1–W–Cp*, 113; C2–W–C6, 117.0(1); C2–W–Cp*, 117; C6–W–Cp*, 125; Cp* denotes the centre of the pentamethylcyclopentadienyl ring.

5 and **6** are distinguished by one absorption of medium intensity at 1584, 1614 and 1610 cm^{-1} , respectively, which can be assigned to the $\nu(\text{C}=\text{N})$ vibration of the iminocarbene ligand. Further support for the assigned structures is given by the ^1H NMR spectra of **2**, **5** and **6**. Thus all complexes are chiral, possessing C_1 symmetry. Therefore the methylene protons of all ethyl groups are diastereotopic, giving rise to two separate doublets of quartets as expected for the AB part of an ABX_3 spin system [$^2J(\text{H}_A\text{H}_B) = 11.7\text{--}12.7$ Hz and $^3J(\text{H}_A\text{H}_X) = ^3J(\text{H}_B\text{H}_X) = 7.3$ Hz] [13]. Furthermore, the ^1H NMR spectra of **5** and **6** show two singlet resonances for the methyl protons of the dimethylamino group at δ 3.62 and 3.65 ppm (**5**) and δ 3.62 and 3.68 ppm (**6**), indicating a hindered rotation of the dimethylamino group about the C(carbene)—N bond as in other aminocarbene complexes [14]. Similarly, two triplet resonances at δ 1.20 and 1.50 ppm are observed for the methyl protons of the inequivalent ethyl groups of **2**. The ^{13}C NMR spectra are also consistent with the proposed structures for **2**, **5** and **6**. Thus all iminocarbene complexes are distinguished by a resonance for the imino-carbon at δ 129.5, 124.7 and 126.1 ppm, respectively. The imino-carbon resonances of **5** and **6** appear at considerably higher field than those of the starting materials (**3**: δ 183.9 ppm; **4**: δ 190.6 ppm) [12]. Furthermore, the iminocarbene complexes **2**, **5** and **6** display a characteristic low-field resonance for the carbene-carbon at δ 221.8, 229.8 and 222.3 ppm, respectively. The carbene-carbon resonances of the tungsten complexes **2** and **6** are accompanied by tungsten satellites [**2**: $^1J(\text{WC}) = 83$ Hz; **6**: $^1J(\text{WC}) = 82$ Hz] arising from $^{183}\text{W}\text{--}^{13}\text{C}$ coupling. Comparable chemical shifts and coupling constants have also been found for other tungsten carbene complexes, such as *cis*- $[\text{Cp}^+(\text{CO})_2(\text{EtNC})\text{W}(\text{C}(\text{H})\text{NEt}_2)]\text{PF}_6$ ($\delta_{\text{C}} = 232.6$ ppm; $^1J(\text{WC}) = 85.4$ Hz) [15] and $[\text{Cp}(\text{CO})_3\text{W}(\text{C}(\text{H})\text{NMe}_2)]\text{BF}_4$ ($\delta_{\text{C}} = 215.5$ ppm; $^1J(\text{WC}) = 70$ Hz) [16]. Finally, two different environments are observed for the inequivalent carbonyl ligands of **2**, **5** and **6**. The CO resonances of the tungsten complexes **2** and **6** display satellites owing to coupling with the ^{183}W nucleus. The $^1J(\text{WC})$ coupling constants (150–161 Hz) are found within the range observed for other tungsten carbonyl complexes [17].

The molecular structure of **2** was determined by a single-crystal X-ray diffraction study. An ORTEP plot of the compound with selected bond lengths and angles is given in Fig. 1.

The W—C(carbene) bond length [W—C6 = 206.5(3) pm] is quite close to those reported for other tungsten carbene complexes, e.g. *trans*- $\text{Cp}(\text{CO})_2(\text{SnPh}_3)\text{--W}(\text{C}(\text{H})\text{Tol})$ [W—C(carbene) = 203.2(7) pm] [18]. The adjacent C(carbene)—N bond [N2—C6 = 132.1(3) pm] is intermediate in length between that expected for a $\text{C}(\text{sp}^2)\text{--N}(\text{sp}^2)$ single (144 pm) and a $\text{C}(\text{sp}^2)\text{--N}(\text{sp}^2)$ double bond (127 pm) [19], indicating that in full

agreement with the ^1H and ^{13}C NMR spectra a high degree of π -bonding exists between the carbene-carbon and amino-nitrogen atom. The sum of the angles around the carbene-carbon is 359.9° , consistent with a sp^2 -hybridized carbon atom. The W—N1 bond length of 220.6(2) pm is close to that reported for other W—N(sp^2) bonds [12b,20], whereas the N1—C4 bond with 131.8(4) pm is slightly longer than a $\text{C}(\text{sp}^2)\text{--N}(\text{sp}^2)$ double bond.

A striking feature of the structure of **2** is the deviation of the four-membered metallacycle from planarity, as demonstrated by the dihedral angle between the planes defined by the atoms W, N1 and C4 and W, C6 and C4 (41.2°), or the dihedral angle between the planes defined by the atoms W, N1 and C6 and N1, C4 and C6 (44.9°). This deviation results in a weak bonding interaction between the tungsten centre and the imino-carbon atom [W...C(4) = 245.4(3) pm]. In addition, the interplanar angle W—C6—N2/C5—C4—C6 of 51.7° excludes π -bonding between the carbene-carbon atom C6 and the imino-carbon atom C4. All these features suggest the presence of a η^3 -bonded iminocarbene ligand in **2** and reveal the electronic similarity of **2**, **5** and **6** with molybdenum(II) and tungsten(II) η^3 -vinylcarbene complexes [21]. Synthetic aspects of this similarity are currently being studied.

3. Experimental details

Standard Schlenk procedures were used for all syntheses and sample manipulations. The solvents were dried by standard methods (n-pentane over CaH_2 ; Et_2O and THF over Na/benzophenone; CH_2Cl_2 over P_2O_5 and Na/Pb alloy; MeCN over P_2O_5 and K_2CO_3), distilled under nitrogen and stored over 4 Å (MeCN over 3 Å) molecular sieves prior to use. The silylated silica used for chromatography (Merck, activity I, 0.063–0.2 mm) was degassed, dried at 150°C in vacuo and then saturated with nitrogen.

Elemental analyses were performed in the Microanalytical Laboratory of the Inorganic Chemistry Department of the TU München. IR spectra were recorded on a Perkin-Elmer 1650 FT-IR spectrophotometer in CH_2Cl_2 . ^1H and ^{13}C NMR spectra were recorded on a JEOL-GX 400 instrument in dry deoxygenated methylene- d_2 chloride at 20°C , unless otherwise stated. Chemical shifts are referenced to residual solvent signals (CD_2Cl_2 , $\delta_{\text{H}} = 5.32$ and $\delta_{\text{C}} = 53.8$ ppm). The methyl and methylene proton resonances of the two inequivalent ethyl groups of **2** were assigned on the basis of double-resonance experiments. Mass spectra were obtained with a Varian MAT 311A spectrometer; m/z values are relative to the ^{98}Mo and ^{184}W isotopes.

Complexes **1**, **3** and **4** were prepared as described previously [11,12]. $[\text{MeC}\equiv\text{NMe}]\text{BF}_4$ was obtained from

MeCN and $[\text{Me}_3\text{O}]\text{BF}_4$ following the procedure of Kent Barefield et al. [22] and stored under nitrogen.

3.1. Preparation of $[\text{Cp}^*(\text{CO})_2\text{W}\{\text{C}(\text{NEt}_2)\text{C}(\text{Me})=\text{NMe}\}]\text{BF}_4$ (2)

A solution consisting of 1.19 g (2.59 mmol) of **1** in 50 ml of CH_2Cl_2 was treated at -78°C with 363 mg (2.54 mmol) of $[\text{MeC}\equiv\text{NMe}]\text{BF}_4$. The mixture was then allowed to warm to room temperature and stirred for 2 h. Completion of the reaction was revealed by IR spectroscopy. The resulting red solution was evaporated to dryness, the residue dissolved in a minimum amount of THF, the solution cooled to -78°C and treated with a cold $\text{Et}_2\text{O}/n$ -pentane mixture (1:1) (-78°C) to precipitate complex **2**. The supernatant light brown solution was decanted off and the red-brown precipitate washed once with cold Et_2O and dried in vacuo. M.p. 131°C (dec.). Yield, 1.13 g (72%). Anal. Found: C, 39.83; H, 5.22; F, 12.93; N, 4.67; W, 30.57%. $\text{C}_{20}\text{H}_{31}\text{BF}_4\text{N}_2\text{O}_2\text{W}$ (602.13) Calc.: C, 39.90; H, 5.19; F, 12.62; N, 4.65; W, 30.53%. IR (CH_2Cl_2) $\nu(\text{cm}^{-1})$: 1986 (vs), 1926 (s) [$\nu(\text{CO})$]; 1584 (m) [$\nu(\text{C}=\text{N})$]. ^1H NMR δ : 1.20 [t, $^3J(\text{HH}) = 7.3$ Hz, 3H, $1 \times \text{Me}$, NEt]; 1.50 [t, $^3J(\text{HH}) = 7.3$ Hz, 3H, $1 \times \text{Me}$, NEt']; 2.06 [s, 15H, C_5Me_5]; 2.35 [s, 3H, CMe]; 3.20 [s, 3H, NMe]; 3.58 [dq, $^2J(\text{HH}) = 12.7$ Hz, $^3J(\text{HH}) = 7.3$ Hz, 1H, CH_AH_B , NEt]; 3.83 [dq, $^2J(\text{HH}) = 12.7$ Hz, $^3J(\text{HH}) = 7.3$ Hz, 1H, CH_AH_B , NEt]; 3.84 [dq, $^2J(\text{HH}) = 12.7$ Hz, $^3J(\text{HH}) = 7.3$ Hz, 1H, CH_AH_B , NEt]; 3.91 [dq, $^2J(\text{HH}) = 12.7$ Hz, $^3J(\text{HH}) = 7.3$ Hz, 1H, CH_AH_B , NEt'] ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR δ : 10.8 [C_5Me_5]; 14.0 [CMe]; 15.4 [$1 \times \text{Me}$, NEt_2]; 16.0 [$1 \times \text{Me}$, NEt_2]; 42.8 [NMe]; 51.6 [$1 \times \text{CH}_2$, NEt_2]; 52.7 [$1 \times \text{CH}_2$, NEt_2]; 107.0 [C_5Me_5]; 129.5 [CMe]; 221.8 [$\text{W}=\text{C}$, $^1J(\text{WC}) = 83$ Hz]; 224.7 [CO , $^1J(\text{WC}) = 150$ Hz]; 224.9 [CO , $^1J(\text{WC}) = 161$ Hz] ppm. FD-MS (CH_2Cl_2) m/z : 515 [M] $^+$.

3.2. Preparation of $[\text{Cp}^*(\text{CO})_2\text{Mo}\{\text{C}(\text{NMe}_2)\text{C}(\text{Me})=\text{NEt}\}]\text{BF}_4$ (5)

A solution consisting of 490 mg (1.23 mmol) of **3** in 50 ml of CH_2Cl_2 was treated at -78°C with 164 mg (1.11 mmol) of $[\text{Me}_3\text{O}]\text{BF}_4$. The mixture was then allowed to warm to room temperature and stirred for 2 h. Completion of the reaction was revealed by IR spectroscopy (replacement of the two $\nu(\text{CO})$ absorptions of the starting material at 1917 and 1819 cm^{-1} by those of the product at 1996 and 1938 cm^{-1}). The resulting dark red solution was concentrated in vacuo, cooled to -78°C and cold n -pentane (-78°C) was slowly added to precipitate complex **5**. The supernatant light brown solution was decanted off and the red-brown precipitate washed once with cold Et_2O (-78°C) and dried in vacuo. M.p. 66°C . Yield, 530 mg (86%). Anal.

Found: C, 45.86; H, 5.81; Mo, 19.32; N, 5.77%. $\text{C}_{19}\text{H}_{29}\text{BF}_4\text{MoN}_2\text{O}_2$ (500.19) Calc.: C, 45.62; H, 5.84; Mo, 19.18; N, 5.60%. IR (CH_2Cl_2) $\nu(\text{cm}^{-1})$: 1996 (vs), 1938 (s) [$\nu(\text{CO})$]; 1614 (m) [$\nu(\text{C}=\text{N})$]. ^1H NMR δ : 1.32 [t, $^3J(\text{HH}) = 7.3$ Hz, 3H, CH_2CH_3]; 1.96 [s, 15H, C_5Me_5]; 2.18 [s, 3H, CMe]; 3.06 [dq, $^2J(\text{HH}) = 12.2$ Hz, $^3J(\text{HH}) = 7.3$ Hz, 1H, $\text{CH}_A\text{H}_B\text{CH}_3$]; 3.24 [dq, $^2J(\text{HH}) = 12.2$ Hz, $^3J(\text{HH}) = 7.3$ Hz, 1H, $\text{CH}_A\text{H}_B\text{CH}_3$]; 3.62 [s, 3H, NMe]; 3.65 [s, 3H, NMe] ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , -60°C) δ : 10.6 [C_5Me_5]; 13.7 [CMe]; 17.8 [CH_2CH_3]; 46.3 [NMe]; 49.5 [NMe]; 49.7 [CH_2CH_3]; 108.3 [C_5Me_5]; 124.7 [CMe]; 229.8 [$\text{Mo}=\text{C}$]; 230.6 [CO]; 234.6 [CO] ppm. FD-MS (CH_2Cl_2) m/z : 415 [M] $^+$.

3.3. Preparation of $[\text{Cp}^*(\text{CO})_2\text{W}\{\text{C}(\text{NMe}_2)\text{C}(\text{Me})=\text{NEt}\}]\text{BF}_4$ (6)

A solution consisting of 210 mg (0.43 mmol) of **4** in 20 ml of CH_2Cl_2 was treated at -78°C with 57 mg (0.39 mmol) of $[\text{Me}_3\text{O}]\text{BF}_4$. The mixture was then allowed to warm to room temperature and stirred for 2 h. Completion of the reaction was revealed by IR spectroscopy (replacement of the two $\nu(\text{CO})$ absorptions of the starting material at 1906 and 1804 cm^{-1} by those of the product at 1988 and 1925 cm^{-1}). The solvent was then removed in vacuo and the residue purified by chromatography on silylated silica at 0°C . Elution with $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ (1:2) gave a red band, which was concentrated in vacuo cooled to -78°C and treated with cold n -pentane (-78°C) to precipitate complex **6**. Red-brown solid. M.p. 64°C . Yield, 210 mg (83%). Anal. Found: C, 38.76; H, 4.70; N, 5.09; W, 31.70%. $\text{C}_{19}\text{H}_{29}\text{BF}_4\text{N}_2\text{O}_2\text{W}$ (588.10) Calc.: C, 38.80; H, 4.97; N, 4.76; W, 31.26%. IR (CH_2Cl_2) $\nu(\text{cm}^{-1})$: 1988 (vs), 1928 (s) [$\nu(\text{CO})$]; 1610 (m) [$\nu(\text{C}=\text{N})$]. ^1H NMR δ : 1.31 [t, $^3J(\text{HH}) = 7.3$ Hz, 3H, CH_2CH_3]; 2.07 [s, 15H, C_5Me_5]; 2.40 [s, 3H, CMe]; 3.10 [dq, $^2J(\text{HH}) = 11.7$ Hz, $^3J(\text{HH}) = 7.3$ Hz, 1H, $\text{CH}_A\text{H}_B\text{CH}_3$]; 3.27 [dq, $^2J(\text{HH}) = 11.7$ Hz, $^3J(\text{HH}) = 7.3$ Hz, 1H, $\text{CH}_A\text{H}_B\text{CH}_3$]; 3.62 [s, 3H, NMe]; 3.68 [s, 3H, NMe] ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR δ : 10.9 [C_5Me_5]; 14.3 [CMe]; 18.6 [CH_2CH_3]; 46.3 [NMe]; 49.5 [NMe]; 50.4 [CH_2CH_3]; 107.3 [C_5Me_5]; 126.1 [CMe]; 222.3 [$\text{W}=\text{C}$, $^1J(\text{WC}) = 82$ Hz]; 223.8 [CO , $^1J(\text{WC}) = 150$ Hz]; 224.6 [CO , $^1J(\text{WC}) = 158$ Hz] ppm. FD-MS (CH_2Cl_2) m/z : 501 [M] $^+$.

3.4. Structure determination of 2

Crystal data for **2**: $\text{C}_{20}\text{H}_{31}\text{BF}_4\text{N}_2\text{O}_2\text{W}$; $M = 602.1$; monoclinic; space group, $P2_1/n$; $a = 892.6(1)$, $b = 2323.9(2)$, $c = 1183.0(1)$ pm, $\beta = 109.79(1)^\circ$; $V = 2309.0 \times 10^6$ pm 3 ; $Z = 4$, $D_c = 1.732$ g cm $^{-3}$; $F(000) = 1184$; $\lambda(\text{Cu K}\alpha) = 154.184$ pm, $\mu = 98.3$ cm $^{-1}$; $T = 193$ K.

All measurements were performed on an Enraf-Nonius CAD4 diffractometer (incident beam, graphite monochromator; $\theta/2\theta$ scans; $\theta_{\max} = 65^\circ$). Unit cell parameters were derived from the diffractometer setting angles for 25 reflections ($79.9^\circ < \theta < 94.8^\circ$) widely separated in reciprocal space. A total of 4315 intensities was collected. Lorentz, polarization, decay and an empirical absorption correction were applied to the raw data. The crystal structure was solved by Patterson methods, 3797 independent data with $I > 0.0$ being used in the refinements. Hydrogen atoms were placed at their calculated positions. Convergence was reached at $R = 0.048$ and $R_w = 0.048$, respectively. Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-401917, the names of the authors and the journal citation.

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