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Synthesis and structure of novel, air-stable carbyne complexes of tungsten

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Abstract

New Fischer type carbyne complexes of tungsten, **L**$(CO)_2W{\equiv}C{-}R/Ar$, **1b**–**7b**, where R = CH_3, Ar = substituted phenyl, and LH = (2-hydroxyphenyl)-bis(3,5-dimethylpyrazolyl)methane, with L^- being a tridentate, uninegative ligand, were synthesized from $W(CO)_6$ via tetraethylammonium acylmetallate salt, as thermally stable and air-stable solids. In another complex, **8b**, the aryl ring is complexed with tricarbonylchromium. Crystal structure of a representative complex was determined to confirm structural assignment.

Keywords: Carbyne complexes; 2-Hydroxyphenyl-bis(3,5-dimethylpyrazolyl)methane; Thermally stable

1. Introduction

Complexes with transition metal–carbon multiple bonds [1] attract a great deal of attention in organometallic chemistry. Transition metal carbene complexes have been extensively studied in the context of methodology development for organic synthesis [1d]. In comparison, chemistry of carbyne complexes has been exploited to a limited extent [2], owing in part to thermal instability of a large number of these complexes. Development of new ligands that would impart thermal stability as well as permit tuning reactivity of metal–carbon triple bond, therefore, remains an important research objective.

The carbyne complexes originally prepared by Fischer [3a] using electrophilic abstraction of methoxide from methoxymethyl carbene complex, feature four CO ligands. Replacement of CO groups with bidentate, chelating ligands enhances thermal stability of resulting complexes [3b]. A one-pot procedure of formal abstraction of oxide from acyl metalates [4] with strong Lewis acids followed by addition of ligand developed by Mayr [5], is a very practical method to prepare such complexes. Stone [6] applied this protocol to prepare a series of $Cp(CO)_2MC{-}Ar$ complexes as well as complexes bearing Tp ligand, viz. $Tp(CO)_2WC{-}Tol$ [$Tp = \eta^3\text{-}HB(C_3H_3N_2)_3$, Tol = *p*-tolyl]. In continuation of our interest in pyrazole-derived chelating ligands [7], we report herein the synthesis and structural characterization of a new class of air-stable and thermally stable Fischer type carbyne complexes.

2. Results and discussion

We identified (2-hydroxyphenyl)-bis(3,5-dimethylpyrazolyl)methane (**LH**) as an unsymmetrical analog of Tp ligand that features two pyrazole donors and a phenoxide anion. Initially, *o*-anisaldehyde was converted to its dimethyl acetal and the –OMe groups were replaced with 3,5-dimethylpyrazole by an acid-catalyzed reaction. Unfortunately, all efforts to cleave the methyl ether of phenol were unsuccessful. Meanwhile Carrano reported

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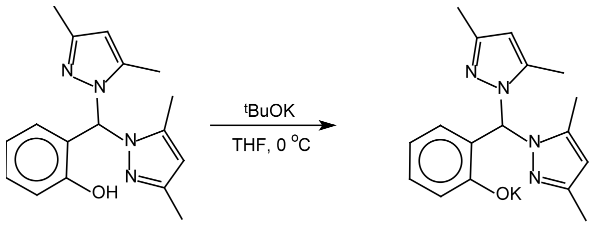


LH LK

Scheme 1.

[8] the synthesis of this ligand by a completely different and direct route from salicylaldehyde and established the coordination ability of the new ligand. The potassium salt of **LH** was prepared by treating a suspension of **LH** in THF with an equivalent amount of potassium *tert*-butoxide at 0 °C (Scheme 1). The cloudy white suspension first became clear within 2–3 min and then a white precipitate of **LK** reappeared from the clear solution. It was isolated and dried thoroughly under vacuum. The salt is hygroscopic but can be stored in a desiccator for several weeks.

The tridentate ligand, **LK**, has a significant difference with Tp ligand. On complexation to a metal ion, the latter forms three six member rings in a tridentate coordination mode with a threefold axis of symmetry. For **LK**, the two pyrazoles would form a six member ring with the metal center, but the phenolate anion would be part of a seven member ring. Overall the complex is expected to have a plane of symmetry. The anionic oxygen donor is expected to occupy the *trans* position with respect to the carbyne fragment and stabilize the complex.

We adopted Mayr's [5] procedure to prepare the carbyne complexes **1b**–**7b** (Scheme 2). Carbyne complexes were obtained as yellow to orange solids.

All carbyne complexes were isolated in good yield (Table 1). They are thermally stable, air-stable in solid state, and do not decompose on prolonged storage at room temperature.

Table 1

Compound	R/Ar	Yield (%)	Dec. (°C)
1b	Me	62	143–145
2b	C_6H_5	74	152–153
3b	2-Me–C_6H_4	66	150–152
4b	4-MeO-2-Me–C_6H_3	58	145–148
5b	2-MeO-4,5-Me_2–C_6H_2	54	148–150
6b	4-MeO–C_6H_4	57	154–156
7b	2,4,6-Me_3–C_6H_2	64	133–135
8b	2-Me–C_6H_4–$Cr(CO)_3$	48	193–196

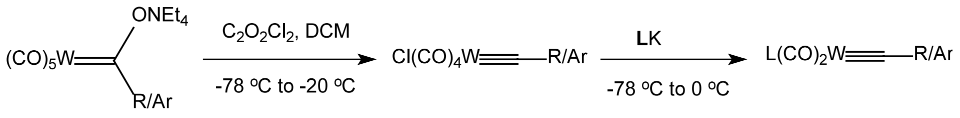
Complex **8b** was synthesized in one-pot from $W(CO)_6$ and (η^6-2-$SnMe_3$-C_6H_4Me)$Cr(CO)_3$ (**8a**) (Scheme 3). Tin–lithium exchange in **8a** was carried out in THF at −78 °C for 2 h. The resulting orange solution was transferred via canula to a suspension of $W(CO)_6$ in ether at −78 °C, which was gradually warmed to 0 °C. Treatment of oxalyl chloride and the ligand in succession led to the formation of the desired product. The orange solid was washed thoroughly with 1:1 dichloromethane:hexane solution to remove residual **8a** and other impurities.

Replacement of two strong π-accepting carbonyl groups from $Cl(CO)_4WC$–R by pyrazole-nitrogen seem to have imparted exceptional stability to these complexes. Selected spectral data are provided in Table 2.

The carbyne complexes have two strong CO absorptions of equal intensity in the infrared spectrum at around 1958–1983 and 1857–1890 cm^{-1}. These values are lower than corresponding Cp or Tp complexes as seen from comparison of absorptions at 1990 and 1919 cm^{-1} of $Cp(CO)_2W{\equiv}C$-(4-tolyl) complex [9] and 1986 and 1903 cm^{-1} of $Tp(CO)_2W{\equiv}C$-(4-tolyl) complex [10] with those of complex **3b** at 1967 and 1877 cm^{-1}. This effect, however, is not reflected in the bond distance parameters (vide infra).

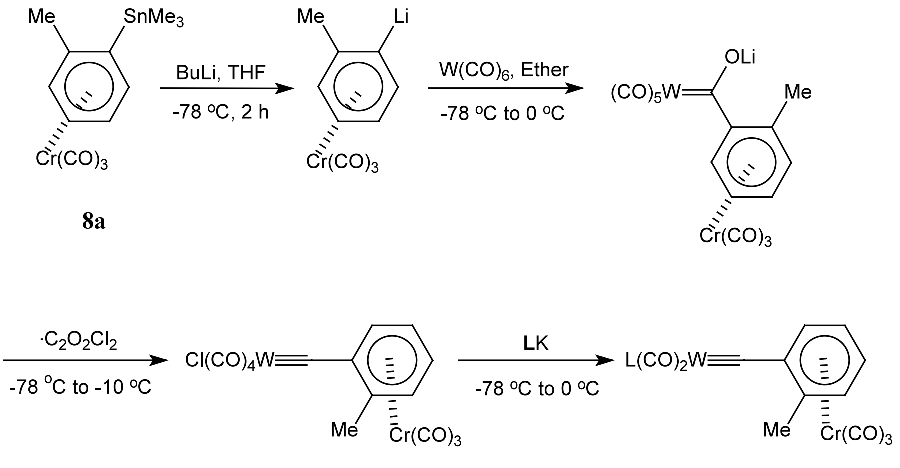
The ^1H-NMR spectra showed symmetrical patterns as expected. Typical six-proton singlets were observed at 2.4–2.5 ppm and 2.6–2.7 ppm for methyl groups of pyrazole. Another singlet at 6.00–6.10 ppm was assigned to pz-H. The benzylic methine of the ligand appears as a singlet at 6.9–7.0 ppm in most cases, sometimes this signal merges with other aromatic protons. However, the ^1H-NMR spectrum of complex **8b** is strikingly different. The symmetry of the molecule is lost because of complexation of the aromatic group with $Cr(CO)_3$ moiety. The two pz-methyl groups (observed as one singlet at 2.6–2.7 ppm in other complexes) appeared at 2.62 and 2.73 ppm as two distinct singlets. Also the two pz-H signals appear separately at 6.08 and 6.10 ppm as singlets.

The ^{13}C-NMR spectra showed the diagnostic peaks for the alkylidyne carbon nuclei at 262–283 ppm. The carbonyl carbons resonate at 222–225 ppm. For complex **8b** the $Cr(CO)_3$ carbon signal was observed at 234



1a-7a 1b-7b

Scheme 2.



8a

8b

Scheme 3.

Table 2
Selected spectroscopic data for complexes **1b**–**8b**

Compound	ν_{CO} (cm^{-1})	^{13}C-NMR peak position (ppm)	
	(CHCl$_3$)	W≡CR	W–CO
1b	1857 (m), 1958 (m)	282.8	222.7
2b	1890 (m), 1979 (m)	271.5	223.6
3b	1877 (m), 1967 (m)	275.2	224.5
4b	1880 (s), 1973 (s)	275.6	224.6
5b	1873 (s), 1967 (s)	270.2	224.7
6b	1886 (s), 1975 (s)	271.3	223.0
7b	1888 (m), 1977 (m)	278.4	224.5
8b	1886 (s), 1948 (s), 1983 (s)	262.9	224.1

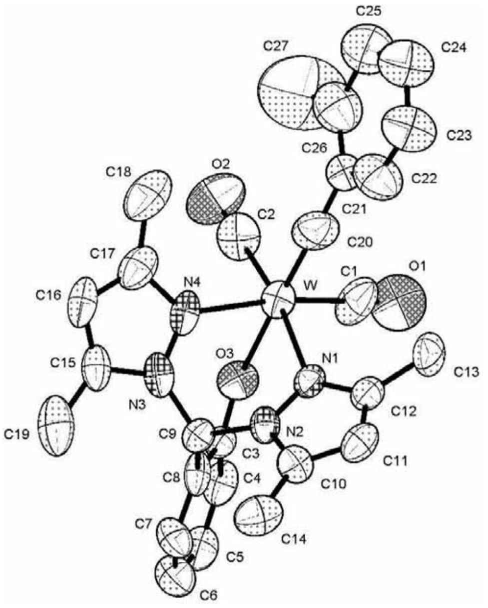


Fig. 1. ORTEP diagram of complex **3b.**

ppm. Interestingly, the carbyne carbon of complex **3b** resonates at 275.2 ppm, whereas the carbyne carbon of **8b** appears at 262.9 ppm. Evidently, coordination of the Cr(CO)$_3$ group to the arene ring results in a somewhat shielded carbyne carbon resonance [6b].

The structure of a representative complex **3b** was confirmed by X-ray analysis. A suitable crystal was grown from acetonitrile at low temperature (−10 °C). The ORTEP diagram of **3b** is displayed in Fig. 1. Selected bond lengths and bond angles are listed in Table 3.

Details of structure determination are included in Section 4 and summarized in Table 4.

As anticipated, the W atom has a distorted octahedral ligand environment with the phenoxide oxygen placed *trans* to the carbyne ligand. The pyrazolyl nitrogen atoms are placed *trans* with respect to the CO ligands. The W–CO bond distances in **3b**, 1.958(19) and 1.971(16) Å, are comparable with 1.94(3) and 1.95(3) Å in [(η^5-C$_5$H$_5$)(CO)$_2$WCC$_6$H$_4$(4-Me)] [9] and with 1.98(5) and 1.97(6) Å in [(CO)$_2$(Bpz$_4$)WCC$_6$H$_4$(4-Me)] where Bpz$_4$ = tetrakis(pyrazolyl)borato ligand [10]. Also, W–N bond distances [2.237(12) and 2.241(11) Å] is similar to those reported. The W≡C bond length is 1.7551(7) Å, which is shorter than most of the other carbyne complexes [1.765(7)–1.878(5) Å] reported earlier [11].

Table 3
Selected bond lengths (Å) and angles (°) for compound **3b**

W–C(20)	1.7551(7)	C(2)–W–C(1)	85.9(8)
W–C(2)	1.958(19)	C(20)–W–O(3)	173.6(3)
W–C(1)	1.971(16)	C(2)–W–O(3)	88.6(6)
W–O(3)	2.148(10)	C(1)–W–O(3)	87.2(7)
W–N(1)	2.237(12)	C(20)–W–N(1)	99.8(3)
W–N(4)	2.241(11)	O(3)–W–N(1)	84.3(4)
C(20)–C(21)	1.4638	C(20)–W–N(4)	102.0(3)
C(20)–W–C(2)	87.8(6)	C(2)–W–N(4)	94.9(6)
C(20)–W–C(1)	87.2(6)	N(1)–W–N(4)	78.9(4)

Table 4
Crystal data and structure refinement for complex **3b**

Empirical formula	$C_{27}H_{26}N_4O_3W$
Formula weight	638.37
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	13.0935(17)
b (Å)	15.030(2)
c (Å)	13.8600(19)
β (°)	98.363(2)
V (Å^3)	2698.7(6)
Z	4
D_{calc} (mg m^{-3})	1.571
Absorption coefficient (mm^{-1})	4.314
$F(0\,0\,0)$	1256
Crystal size (mm)	0.34 × 0.07 × 0.06
θ range for data collection (°)	2.01–25.00
Limiting indices	$-15 \leqslant h \leqslant 10$, $-17 \leqslant k \leqslant 17$, $-16 \leqslant l \leqslant 16$
Reflections collected/unique	13 121/4740 [$R_{int} = 0.0874$]
Completeness to $\theta = 25.00$	99.6%
Max/min transmission	0.7942, 0.3176
Refinement method	Full-matrix-block least-squares on F^2
Data/restraints/parameters	4740/4/321
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0826$, $wR_2 = 0.1826$
R indices (all data)	$R_1 = 0.1478$, $wR_2 = 0.2039$
Goodness-of-fit on F^2	1.060
Largest difference peak and hole (e Å^{-3})	1.974 and −1.516

3. Conclusion

In summary, we have described a set of Fischer type carbyne complexes that are air-stable as well as thermally stable. We have used a ligand, **L**H, which coordinates through two pyrazole nitrogens and a phenoxide anion. In this respect it is an analog of Tp ligand and isoelectronic with Cp ligand as well. Structural assignment was confirmed by crystal structure determination of a representative complex. Improving the ligand design to ensure better solubility of these complexes, introduction of chirality and exploration of reactivity of the metal–carbon triple bond are currently being pursued in our laboratory.

4. Experimental

All reactions were carried out under an atmosphere of argon. Dichloromethane was distilled from calcium hydride under argon. Tetrahydrofuran was distilled under argon from sodium and benzophenone. Acyl pentacarbonyl metal complexes $Et_4N^+[(CO)_5WC(O)R]^-$ (**1a**–**7a**) were synthesized by literature method [12]. $Cr(CO)_3(\eta^6\text{-}2\text{-}SnMe_3\text{–}C_6H_4Me)$ (**8a**) was prepared by thermolysis of 2-trimethylstannyltolune and chromium hexacarbonyl [13]. All other reagents were purchased from commercial suppliers and used as received. Infrared spectra were recorded on a Shimadzu FTIR-8400 spectrometer and absorptions are expressed in cm^{-1}. All ^{1}H and ^{13}C-NMR spectra were obtained on a Bruker AC200, MSL300 or DRX500 spectrometer. Elemental analyses were obtained on Carlo-Ebra 1100 automatic analyzer. Melting points were recorded on a Thermonik Campbell melting point apparatus and are uncorrected.

4.1. Preparation of complexes *1b*–*7b*

To a cold solution (−78 °C) of **1a** (320 mg, 0.64 mmol) in dichloromethane (6 ml), was added a cold (−78 °C) solution of oxalyl chloride (0.06 ml, 0.67 mmol) in dichloromethane (1 ml). The color of the solution changed instantly from orange–yellow to dark red. The reaction mixture was allowed to come to −20 °C over a period of 2 h, during which time the color changed to orange–brown. The solution was again cooled to −78 °C and ligand **L**K (224 mg, 0.67 mmol) was added in one portion at that temperature. The temperature was then allowed to come to 0 °C over a period of 2 h. Solvent was removed in vacuo and the residue was suspended in a small volume of dichloromethane and filtered through a small pad of alumina using dichloromethane as eluant. Evaporation of solvent afforded complex **1b** (223 mg, 62%) as a pale yellow solid (dec. point 143–145 °C). ^{1}H-NMR (CD_2Cl_2, 200 MHz): δ 7.12–6.90 (m, 2H, Ph*H*), 6.87 (s, 1H, Bz*H*), 6.48 (d, 1H, $J = 7.2$ Hz Ph*H*), 6.37 (t, 1H, $J = 7.2$ Hz, Ph*H*), 6.05 (s, 2H, pzC*H*), 2.66 (s, 6H, pzCC*H*$_3$), 2.41 (s, 6H, pzCC*H*$_3$), 2.24 (s, 3H, WCC*H*$_3$). ^{13}C-NMR (CD_2Cl_2, 75.5 MHz): δ 282.8 (W≡*C*), 222.7 (W*C*O), 166.8, 154.0, 141.4, 132.6, 129.8, 123.5, 122.1, 113.7, 108.1 (Ph*C* and pz*C*), 72.4 (Bz*C*), 37.4 (WC*C*H$_3$), 17.5 (pzC*C*H$_3$), 12.3 (pzC*C*H$_3$). Anal. Calc. for $C_{21}H_{22}N_4O_3W$: C, 44.84; H, 3.91; N, 9.96. Found C, 44.81; H, 4.02; N, 9.91.

Complexes **2b**–**7b** were similarly prepared in ca. 0.5–0.7 mmol scale.

Complex **2b**: Orange–yellow solid, 74% (dec. point 152–153 °C). ^{1}H-NMR ($CDCl_3$, 200 MHz): δ 7.30–7.06 (m, 6H, Ph*H*), 7.01–6.91 (m, 2H, Ph*H* and Bz*H*), 6.65 (d, 1H, $J = 7.1$ Hz, Ph*H*), 6.43 (t, 1H, $J = 7.1$ Hz, Ph*H*), 6.06 (s, 2H, pzC*H*), 2.69 (s, 6H, pzCC*H*$_3$), 2.48 (s, 6H, pzCC*H*$_3$). ^{13}C-NMR (CD_2Cl_2, 75.5 MHz): δ 271.5 (W≡*C*), 223.6 (W*C*O), 166.4, 154.3, 151.3, 141.6, 132.6, 129.8, 129.1, 128.4, 127.1, 123.7, 122.3, 114.2, 108.2 (Ph*C* and pz*C*), 72.3 (Bz*C*), 17.6 (pzC*C*H$_3$), 12.3 (pzC*C*H$_3$). Anal. Calc. for $C_{26}H_{24}N_4O_3W$: C, 50.00; H, 3.85; N, 8.97. Found C, 50.09; H, 4.02; N, 8.87.

Complex **3b**: Orange–yellow solid, 66% (150–152 °C). ^{1}H-NMR (CD_2Cl_2, 300 MHz): δ 7.18–7.00 (m, 6H, Ph*H*), 6.99 (s, 1H, Bz*H*), 6.51 (d, 1H, $J = 7.2$

Hz, Ph*H*), 6.43 (t, 1H, *J* = 7.2 Hz, Ph*H*), 6.09 (s, 2H, pzC*H*), 2.57 (s, 6H, pzCC*H*$_3$), 2.50 (s, 6H, pzCC*H*$_3$), 2.22 (s, 3H, PhC*H*$_3$). ^{13}C-NMR (CD_2Cl_2, 75.5 MHz): δ 275.2 (W≡*C*), 224.5 (W*C*O), 166.6, 154.2, 149.7, 141.4, 138.9, 132.6, 130.7, 130.0, 126.9, 125.7, 123.6, 122.5, 114.1, 108.0 (Ph*C* and pz*C*), 72.4 (Bz*C*), 19.8 (Ph*C*H$_3$) 17.5 (pzC*C*H$_3$), 12.4 (pzC*C*H$_3$). Anal. Calc. for $C_{27}H_{26}N_4O_3W$: C, 50.78; H, 4.07; N, 8.78. Found C, 50.97; H, 4.17; N, 8.67.

Complex **4b**: Orange solid, 58% (dec. point 145–148 °C). ^{1}H-NMR ($CDCl_3$, 200 MHz): δ 7.21–7.06 (m, 2H, Ph*H*), 7.04–6.94 (m, 2H, Ph*H* and Bz*H*), 6.71–6.55 (m, 2H, Ph*H*), 6.54 (s, 1H, Ph*H*), 6.41 (t, 1H, *J* = 7.2 Hz, Ph*H*), 6.03 (s, 2H, pzC*H*), 3.75 (s, 3H, OC*H*$_3$), 2.61 (s, 6H, pzCC*H*$_3$), 2.50 (s, 6H, pzCC*H*$_3$), 2.26 (s, 3H, PhC*H*$_3$). ^{13}C-NMR (CD_2Cl_2, 75.5 MHz): δ 275.6 (W≡*C*), 224.6 (W*C*O), 166.7, 158.8, 154.2, 143.6, 141.4, 140.9, 133.2, 132.2, 130.7, 123.6, 122.4, 115.3, 114.0, 111.1, 108.0 (Ph*C* and pz*C*), 72.4 (Bz*C*), 55.7 (O*C*H$_3$), 20.1 (Ph*C*H$_3$) 17.4 (pzC*C*H$_3$), 12.4 (pzC*C*H$_3$). Anal. Calc. for $C_{28}H_{28}N_4O_4W$: C, 50.29; H, 4.19; N, 8.38. Found C, 50.07; H, 4.37; N, 8.27.

Complex **5b**: Orange solid, 54% (dec. point 148–150 °C). ^{1}H-NMR ($CDCl_3$, 200 MHz): δ 7.11 (t, 1H, *J* = 6 Hz, Ph*H*), 7.05–6.84 (m, 3H, Ph*H* and Bz*H*), 6.65 (d, 1H, *J* = 8 Hz, Ph*H*), 6.53 (s, 1H, Ph*H*), 6.40 (t, 1H, *J* = 8 Hz, Ph*H*), 6.03 (s, 2H, pzC*H*), 3.72 (s, 3H, OC*H*$_3$), 2.72 (s, 6H, pzCC*H*$_3$), 2.47 (s, 6H, pzCC*H*$_3$), 2.17 (s, 3H, PhC*H*$_3$) 2.11 (s, 3H, PhC*H*$_3$). ^{13}C-NMR (CD_2Cl_2, 50.3 MHz): δ 270.2 (W≡*C*), 224.7 (W*C*O), 166.9, 158.7, 154.7, 141.5, 138.3, 137.6, 132.6, 132.2, 129.8, 128.4, 123.9, 122.4, 113.9, 113.1, 108.2 (Ph*C* and pz*C*), 72.5 (Bz*C*), 55.8 (O*C*H$_3$), 20.6 (Ph*C*H$_3$), 19.0 (Ph*C*H$_3$), 17.5 (pzC*C*H$_3$), 12.4 (pzC*C*H$_3$). Anal. Calc. for $C_{29}H_{30}N_4O_4W$: C, 51.03; H, 4.40; N, 8.21. Found C, 50.89; H, 4.43; N, 7.99.

Complex **6b**: Orange solid, 57% (dec. point 154–156 °C). ^{1}H-NMR ($CDCl_3$, 200 MHz): δ 7.22 (d, 2H, *J* = 8.6 Hz, Ph*H*), 7.12 (t, 1H, *J* = 7.4 Hz, Ph*H*), 7.04–6.94 (m, 2H, Ph*H* and Bz*H*), 6.73 (d, 2H, *J* = 8.6 Hz, Ph*H*), 6.65 (d, 1H, *J* = 8 Hz, Ph*H*), 6.41 (t, 1H, *J* = 7.4 Hz, Ph*H*), 6.05 (s, 2H, pzC*H*), 3.77 (s, 3H, OC*H*$_3$), 2.70 (s, 6H, pzCC*H*$_3$), 2.47 (s, 6H, pzCC*H*$_3$). ^{13}C-NMR ($CDCl_3$, 50.3 MHz): δ 271.3 (W≡*C*), 223.1 (W*C*O), 166.5, 158.5, 153.9, 145.0, 140.7, 132.3, 130.5, 129.1, 123.9, 122.0, 113.5, 107.9 (Ph*C* and pz*C*), 72.2 (Bz*C*), 55.5 (O*C*H$_3$), 17.5 (pzC*C*H$_3$), 12.2 (pzC*C*H$_3$). Anal. Calc. for $C_{27}H_{26}N_4O_4W$: C, 49.54; H, 3.97; N, 8.56. Found C, 49.45; H, 3.92; N, 8.82.

Complex **7b**: Yellow solid, 64% (dec. point 133–135 °C). ^{1}H-NMR ($CDCl_3$, 200 MHz): δ 7.12 (t, 2H, *J* = 7 Hz, Ph*H*), 7.04–6.93 (m, 2H, Ph*H* and Bz*H*), 6.71–6.60 (m, 3H, Ph*H*), 6.42 (t, 1H, *J* = 7 Hz, Ph*H*), 6.02 (s, 2H, pzC*H*), 2.59 (s, 6H, pzCC*H*$_3$), 2.50 (s, 6H, pzCC*H*$_3$), 2.15 (bs, 9H, PhC*H*$_3$). ^{13}C-NMR (CD_2Cl_2, 50.3 MHz): δ 278.4 (W≡*C*), 224.5 (W*C*O), 154.5, 141.4, 140.4, 136.9, 132.6, 129.8, 128.2, 123.7, 122.6, 114.0, 108.0 (Ph*C* and pz*C*), 72.6 (Bz*C*), 21.7 (Ph*C*H$_3$), 20.0 (Ph*C*H$_3$), 17.6 (pzC*C*H$_3$), 12.4 (pzC*C*H$_3$). Anal. Calc. for $C_{29}H_{30}N_4O_3W$: C, 52.25; H, 4.50; N, 8.41. Found C, 51.98; H, 4.51; N, 8.27.

4.2. *Preparation of complex* ***8b***

To a solution of compound **8a** (340 mg, 0.87 mmol) in tetrahydrofuran (10 ml) at −78 °C, was added ^{n}BuLi (1.6 M in hexane, 0.65 ml, 1.04 mmol) and allowed to react for 2 h at this temperature. The resulting orange solution was added to a suspension of $W(CO)_6$ in ether at −78 °C. The reaction mixture was allowed to come to 0 °C over a period of 2 h during which time $W(CO)_6$ dissolved and color of the solution changed to orange–red. The reaction mixture was again cooled to −78 °C and a cold solution of (−78 °C) oxalyl chloride (0.08 ml, 0.91 mmol) in tetrahydrofuran (2 ml) was added to it. An immediate darkening of color to deep red was observed. The reaction mixture was warmed up to −10 °C resulting in an orange–brown solution. It was again cooled to −78 °C and the ligand **LK** (305 mg, 0.91 mmol) was added and allowed to come to 0 °C over a period of 2 h. The resulting suspension was filtered through a small alumina column using dichloromethane as eluant. Solvent removed and the orange solid thus obtained was washed thoroughly with 1:1 dichloromethane:hexane solution to remove unreacted **8a** and other impurities. Complex **8b** (323 mg, 48%) was obtained as an orange solid (dec. point 193–196 °C). ^{1}H-NMR (CD_2Cl_2, 500 MHz): δ 7.05 (t, 1H, *J* = 7.5 Hz, Ph*H*), 6.99 (d, 1H, *J* = 7.5 Hz, Ph*H*), 6.94 (s, 1H, Bz*H*) 6.46 (d, 1H, *J* = 7.2 Hz, Ph*H*), 6.40 (t, 1H, *J* = 7.2 Hz, Ph*H*), 6.10 (s, 1H, pzC*H*), 6.08 (s, 1H, pzC*H*), 5.53 (d, 1H, *J* = 6.3 Hz, Cr(CO)$_3$Ar*H*), 5.40 (t, 1H, *J* = 6.3 Hz, Cr(CO)$_3$Ar*H*), 5.01(t, 1H, *J* = 6.3 Hz, Cr(CO)$_3$Ar*H*), 4.95 (d, 1H, *J* = 6.3 Hz, Cr(CO)$_3$Ar*H*), 2.73 (s, 3H, pzCC*H*$_3$), 2.62 (s, 3H, pzCC*H*$_3$), 2.47 (s, 6H, pzCC*H*$_3$), 2.10 (s, 3H, PhC*H*$_3$). ^{13}C-NMR (CD_2Cl_2, 50.3 MHz): δ 262.9 (W≡*C*), 234.2 (Cr*C*O) 224.1 (W*C*O), 166.3, 154.6, 141.7, 132.7, 129.7, 123.8, 122.8, 114.6, 108.2 (Ph*C* and pz*C*), 98.5, 94.8, 91.7, 88.2 (Cr(CO)$_3$Ar*C*), 72.4 (Bz*C*), 19.7 (Cr(CO)$_3$Ar*C*H$_3$), 17.8 (pzC*C*H$_3$), 12.4 (pzC*C*H$_3$). Anal. Calc. for $C_{30}H_{26}N_4O_6CrW$: C, 46.51; H, 3.36; N, 7.23. Found C, 46.40; H, 3.42; N, 7.33.

4.3. *X-ray crystal structure analysis for complex* ***3b***

Single crystal of the complex was grown from acetonitrile. An orange colored thin crystal of approximate size 0.34 × 0.07 × 0.06 mm, was used for data collection on Bruker SMART APEX CCD diffractometer using Mo–K$_\alpha$ radiation with fine focus tube with 50 kV and 40 mA. Crystal to detector distance 6.05 cm, 512 × 512 pixels frame^{-1}, hemisphere data acquisition.

Total scans = 3, total frames = 1271, Oscillation/frame −0.3°, exposure/frame = 50.0 s frame^{-1}, maximum detector swing angle = −30.0°, beam center = (260.2, 252.5), in plane spot width = 1.24, SAINT integration, 2θ range = 2.01–25.00°, completeness to 2θ of 25° is 99.6%. SADABS correction applied, $C_{27}H_{26}N_4O_3W$ $M = 638.37$. Crystals belong to monoclinic, space group $P2_1/c$, $a = 13.094$ (2), $b = 15.031(2)$, $c = 13.860$ (2) Å, $\beta = 98.363$ (2)°, $V = 2698.7(6)$ Å^3, $Z = 4$, $D_{calc} = 1.571$ mg m^{-3}, μ (Mo–K$_\alpha$) = 4.314 mm^{-1}, $T = 293(2)$ K, 13 118 reflections measured, 4740 unique [$I > 2\sigma(I)$], R value 0.0826, $wR_2 = 0.1828$. All the data were corrected for Lorentzian, polarization and absorption effects. SHELX-97 (ShelxTL) [14] was used for structure solution and full matrix least squares refinement on F^2. Hydrogen atoms were included in the refinement as per the riding model. The R value of 0.0826 is due to the highly disordered 2-tolyl group. Tolyl group atoms shows unusually high thermal anisotropy with ellipsoid elongated perpendicular to the plane of the ring. Modeling this disorder over various occupancies did not yield convergence. However, after the first few cycles of refinement using FLAT, this group was kept fixed during the refinement. Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 198105.

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References

[1] (a) W.A. Nugent, J.M. Mayer, Metal Ligand Multiple Bond, Wiley, New York, 1988;
(b) K.H. Dötz, H. Fischer, P. Hofman, F.R. Kreissl, U. Schubert, K. Weiss, Transition Metal Carbene Complexes, Verlag Chemie, Weinheim, 1983;
(c) H. Fischer, P. Hofman, F.R. Kreissl, R.R. Shrock, U. Schubert, K. Weiss, Carbyne Complexes, VCH, New York, 1988;
(d) F.Z. Doerwald, Metal Carbenes in Organic Synthesis, Wiley-VCH, Weinheim, 1998.

[2] (a) B.E. Woodworth, P.S. White, J.L. Templeton, J. Am. Chem. Soc. 120 (1998) 9028;
(b) B.E. Woodworth, D.S. Frohnhapfel, P.S. White, J.L. Templeton, Organometallics 17 (1998) 1655;
(c) D.S. Frohnhapfel, P.S. White, J.L. Templeton, Organometallics 19 (2000) 1497;
(d) A.E. Enriquez, P.S. White, J.L. Templeton, J. Am. Chem. Soc. 123 (2001) 4992;
(e) A.E. Enriquez, J.L. Templeton, Organometallics 21 (2002) 852;
(f) B. Schwenzer, J. Schleu, N. Burzlaff, C. Karl, H. Fischer, J. Organomet. Chem. 641 (2002) 134 (For recent work on carbyne chemistry).

[3] (a) E.O. Fischer, G. Kreis, C.G. Kreiter, J. Müller, G. Huttner, H. Lorenz, Angew. Chem. Int. Ed. Engl. 12 (1973) 564;
(b) E.O. Fischer, A. Ruhs, F.R. Kreissl, Chem. Ber. 110 (1977) 805.

[4] H. Fischer, E.O. Fischer, J. Organomet. Chem. 69 (1974) C1.

[5] G.A. McDermott, A.M. Dorries, A. Mayr, Organometallics 6 (1987) 925.

[6] (a) S.J. Dossett, A.F. Hill, J.C. Jeffery, F. Marken, P. Sherwood, F.G.A. Stone, J. Chem. Soc. Dalton Trans. (1988) 2453;
(b) J.R. Fernández, F.G.A. Stone, J. Chem. Soc. Dalton Trans. (1988) 3035;
(c) I.J. Hart, A.F. Hill, F.G.A. Stone, J. Chem. Soc. Dalton Trans. (1989) 2261.

[7] (a) V.S. Joshi, A. Sarkar, P.R. Rajamohanan, J. Organomet. Chem. 409 (1991) 341;
(b) V.S. Joshi, V.K. Kale, K.M. Sathe, A. Sarkar, S.S. Tavale, C.G. Suresh, Organometallics 10 (1991) 2898;
(c) V.S. Joshi, M. Nandi, H. Zhang, B.S. Haggerty, A. Sarkar, Inorg. Chem. 32 (1993) 1301;
(d) S.K. Chowdhury, V.S. Joshi, A.G. Samuel, V.G. Puranik, S.S. Tavale, A. Sarkar, Organometallics 13 (1994) 4092;
(e) V.S. Joshi, K.M. Sathe, M. Nandi, P. Chakrabarti, A. Sarkar, J. Organomet. Chem. 485 (1995) C1;
(f) S.K. Chowdhury, M. Nandi, V.S. Joshi, A. Sarkar, Organometallics 16 (1997) 1806;
(g) S.K. Chowdhury, U. Samanta, V.G. Puranik, A. Sarkar, Organometallics 16 (1997) 2618;
(h) V.S. Joshi, S.K. Chowdhury, A. Sarkar, Proc. Ind. Acad. Sci. 107 (1995) 447 (For a short review of non-boron pyrazole-derived chelates).

[8] T.C. Higgs, C.J. Carrano, Inorg. Chem. 36 (1997) 291.

[9] E.O. Fischer, T.L. Lindner, G. Huttner, P. Friedrich, F.R. Kreiβl, J.O. Besenhard, Chem. Ber. 110 (1977) 3397.

[10] M. Green, J.A.K. Howard, A.P. James, A.N.M. Jelfs, C.M. Nunn, F.G.A. Stone, J. Chem. Soc. Chem. Commun. (1984) 1623.

[11] A. Mayr, H. Hoffmeister, Adv. Organomet. Chem. 32 (1993) 227 (For a collection of data).

[12] E.O. Fischer, R. Aumann, Chem. Ber. 101 (1968) 954.

[13] C.A.L. Mahaffy, P.L. Pauson, Inorg. Synth. 19 (1979) 154.

[14] G.M. Sheldrick, SHELX-97 Program for Crystal Structure Solution and Refinement, University of Göttingen, Germany, 1997.