

First examples of dipyrido[1,2-c:2',1'-e]imidazolin-7-ylidenes serving as NHC-ligands: Synthesis, properties and structural features of their chromium and tungsten pentacarbonyl complexes

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Dedicated to Professor Günter Helmchen on the occasion of his 65th birthday.

Abstract

The first use of dipyridocarbenes as Arduengo–Wanzlick type carbene ligands for transition metal complexes is reported. The complexes $M(\text{CO})_5\text{L}$ (L = dipyridoimidazolinylidene, di-*tert*-butyldipyridoimidazolinylidene, M = Cr, W) were synthesized and their spectroscopic and structural properties compared with the literature known *N*-heterocyclic carbene (NHC) group 6 metal pentacarbonyl complexes. This reveals that the ^{13}C NMR carbene signals of these complexes with dipyrido carbene ligands show the strongest high-field shift ever observed for $M(\text{CO})_5(\text{NHC})$ (M = Cr, W) complexes. The structural characterization shows alternating single and double bonds in the conjugated dipyrido moiety of the ligand.

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1. Introduction

Arduengo–Wanzlick carbenes [1] have gained an important role as ligands for transition metal complexes [2], due to their unique qualities as strong σ -donor and poor π -acceptor ligands [3]. This leads to a higher activity in many transition metal catalysts, most prominent example is the second generation of Grubbs catalysts for the olefin metathesis reaction [4]. A lot of effort is made to tailor new *N*-heterocyclic carbenes (NHCs) for fine-tuning their properties by varying ring-size, hetero atoms and substituents [5]. The “classical” Arduengo–Wanzlick carbenes can be divided into three main types:

imidazolidinylienes **I** [6], benzimidazolinylienes **II** [7], and the unsaturated imidazolinylienes **III** [8] (Fig. 1).

Interestingly the benzimidazolinylienes **II** show electronic properties more similar to the saturated carbenes **I** than to the unsaturated **III**. This can be explained by the tendency of the annelated benzene ring to maintain its aromatic stabilisation.

A dipyridoimidazolinylidene **V** first reported by Weiss et al. [9] has caught our interest, because the empty p-orbital of this singlet carbene is in conjugation with a 14 electron conjugated π -system of the dipyrido moiety. Thus an additional stabilization of the empty p-orbital of the carbene can be expected. The dipyrido-carbene was reported by Weiss to be only stable at -30°C and was characterized by ^{13}C NMR spectroscopy, reaction with sulfur and selenium and ab initio calculations. The monopyridocarben **IV** and its Rh and Ir complexes were very recently synthesized by

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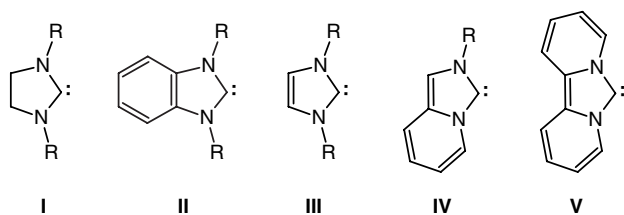


Fig. 1. Various types of the “classical” *N*-heterocyclic carbenes **I–III** and the mono-**IV** and dipyridocarbene **V**.

Lassaletta and coworkers [10], but to our knowledge no use of the dipyridocarbene **V** as a ligand for transition metal complexes was reported in literature so far.¹ This might be due to the synthesis of the dipyridoimidazolium salts that requires a multistep synthesis of an arsonium salt. We found it more convenient to use the synthesis reported by Sasse and coworkers [11] for the dipyridoimidazolium salts **1a** and **1b** in the 1960s. With this known procedure our goal was to synthesize the first metal complexes with dipyridocarbenes as a ligand and to investigate the properties of this ligand and its complexes. For a proper comparison with other NHC complexes we have synthesized their pentacarbonyl complexes of chromium **3a,b** and tungsten **4**.

2. Results and discussion

2.1. Synthesis and characterization of the dipyridocarbene complexes **3a,b** and **4**

Due to the thermic lability of the free carbenes **2a–b**, the complexes were synthesized (Scheme 1) by generating the carbene in situ at $-30\text{ }^{\circ}\text{C}$ by reaction of the imidazolium salt **1** with sodium-*tert*-butanolate in tetrahydrofuran and passing the solution through a glass filter that was charged with Celite[®] and cooled to $-30\text{ }^{\circ}\text{C}$ to remove sodium chloride. The solution was dropped into a tetrahydrofuran solution of chromium- or tungstenpentacarbonyltetrahydrofuran generated in situ by photolysis and cooled to $-30\text{ }^{\circ}\text{C}$. The mixture was stirred for 24 h at rt and after workup the complexes were purified by filtration over silica gel to give the complexes **3a,b** and **4** as yellow solids in good yields.

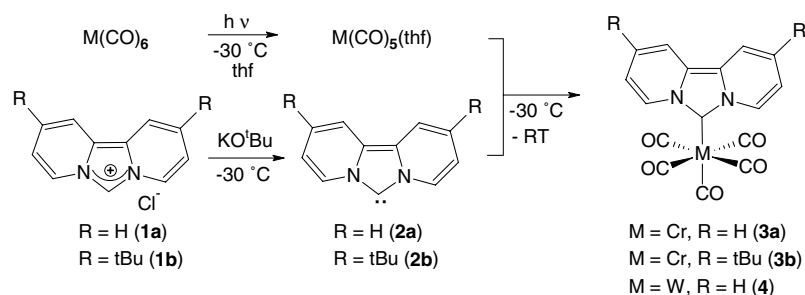
The ¹³C NMR spectra of the complexes reveal the signals of the carbene C atom at δ 171 (**3a**), 168 (**3b**), and 160 (**4**). To our knowledge, this is the strongest high-field shift reported for *N*-heterocyclic carbene ligands at chromium or tungsten pentacarbonyl frag-

ments. The chemical shifts of $\text{Cr}(\text{CO})_5(\text{NHC})$ complexes with saturated NHC ligands **I** lie in a typical range of 210–225 (Cr) and 200–210 ppm (W) [3c,12] with benzimidazolylidenes **II** between 205–210 (Cr) and 195–200 ppm (W) [13] and with unsaturated NHCs **III** at 185–195 (Cr) and 175–185 ppm (W) [3a]. The high-field shift of the carbene signal of about 15 ppm in the complexes **3a,b** and **4** is also observed for the free carbenes **2a** (198 ppm) and **2b** (196 ppm) compared to 235–245 ppm for saturated carbenes **I** [6], 225–235 ppm for benzimidazolylidenes **II** [7] and 205–220 ppm for unsaturated carbenes **III** [8]. The monopyridocarbenes **VI** show – as expected – a chemical shift in between the unsaturated carbene **III** and the dipyridocarbene **V** of 206–209 ppm. We believe that this high-field shift is due to conjugation of the empty carbene p-orbital with the conjugated 14 electron π -system thus increasing the electron density at the carbene atom which leads to a stronger shielding of the magnetic field than in other NHCs.

The result of a strong σ -donor and weak π -acceptor capability of *N*-heterocyclic carbenes is a stronger π -back donation from the metal to the *trans*-carbonyl ligand which is displayed by a lower CO stretching frequency in the IR spectrum. The lower the stretching frequency, the better is the combination of strong σ -donor and weak π -acceptor capability of the carbene ligand. Unfortunately, a separate discrimination of those two properties by IR is not possible. The IR stretching frequencies of the new dipyridocarbene complexes **3a** and **3b** were measured as KBr pellets and in the case of **3b** also as a solution spectrum in *n*-hexane to compare it with the literature known chromiumpentacarbonyl complexes **VI–VIII** (Fig. 2).

The total symmetric stretching frequency is almost independent from the media (**3b**: $\nu = 2053$ (KBr), 2055 cm^{-1} ; (*n*-hexane)) and an influence of the *t*-butyl substituent is not observed as the data (KBr) for **3a** and **3b** are identical. The total symmetric stretching frequency at $\nu = 2053\text{ cm}^{-1}$ is slightly smaller than observed by Hahn et al. [13] for the benzimidazolylidene complex **VII** (M = Cr) (KBr, $\nu = 2057\text{ cm}^{-1}$), which is also found for the respective tungsten complexes (**4**: $\nu = 2060\text{ cm}^{-1}$; **VII** (M = W): $\nu = 2063\text{ cm}^{-1}$). A slightly bigger difference is observed for the carbene complex **VI** ($\nu = 2061\text{ cm}^{-1}$) bearing a saturated carbene ligand [14], whereas the stretching frequencies of complex **VIII** with an unsaturated carbene ligand and **3b** are identical (**3b**: $\nu = 2055\text{ cm}^{-1}$, **X**: $\nu = 2056\text{ cm}^{-1}$ (*n*-hexane)) [3c]. Though the saturated carbenes are more σ -basic than unsaturated, they are at the same time more π -acidic and therefore lead to a higher CO stretching frequency [15]. As the substituents at the carbene N-atoms also have a strong influence on the calculated CO stretching frequencies of about $\Delta\nu = 15\text{ cm}^{-1}$, a conclusion of the σ -donor/ π -acceptor capability of the dipyridocarbenes

¹ After acceptance of this paper Prof. Robert Weiss kindly informed us that his coworkers have made Cr and W pentacarbonyl and Pd (II) complexes with carbene **V** and described them only in their dissertations, which were unknown to us: (Cr, W): Frank Jellen, Dissertation, Universität Erlangen (2002); (Pd): Silvia Reichel, Dissertation, Universität Erlangen (1998).

Scheme 1. Synthesis of the chromium and tungsten dipyrido-pentacarbonyl complexes **3a,b** and **4**.

Complex	CO stretching frequencies (cm ⁻¹)	Notes
VI	2061, 1928	
VII	2057, 1980, 1903 (M = Cr)	
VIII	2056, 1925	
3a,b,4	2055, 1927 (3b)	(n-hexane)
3a,b,4	2053, 1970, 1899 (3a)	(KBr)
3a,b,4	2053, 1971, 1900 (3b)	(KBr)
3a,b,4	2063, 1977, 1900 (M = W)	
3a,b,4	2060, 1947, 1899 (4)	(KBr)

Fig. 2. Comparison of the CO stretching frequencies of the literature known complexes **VI–VIII** with the dipyrido complexes **3a,b** and **4**.

V compared to the carbenes **I–III** (Fig. 1) on the basis of the IR data of their chromium pentacarbonyl complexes is not appropriate, but a possibly weaker π -accepting capability of the carbene due to conjugation of the empty carbene p-orbital with the 14 electron dipyrido π -system is not inconsistent with the observed IR data.

2.2. Molecular structures of the complexes **3a** and **4**

The structures of complexes **3a** and **4** were determined by single-crystal X-ray diffraction (Table 1). Compound **3a** (Cr) shows a Cr1–C7 bond length of 2.131(2) Å. This lies in the typical range 2.13–2.16 Å for a chromium–carbene bond in NHC–chromium–pentacarbonyl complexes [3c,13,16]. The Cr1–C10 (1.868(2) Å) and C10–O10 (1.143(3) Å) distances of the *trans*-CO ligand are also similar to those found in other chromium(NHC)pentacarbonyl complexes. As found typical for carbene–(group 6)–pentacarbonyl complexes the NHC ligand is oriented in a staggered conformation with the *cis*-CO ligands [17] (see Fig. 3).

Also interesting is the structure of the carbene ligand itself. The bond lengths of the planar ligand are not of aromatic character as it would be expected, but alternating single and double bonds are observed (N1–C6: 1.389(2); C6–C5: 1.348(2); C5–C4: 1.424(2); C4–C3: 1.353(2); C3–C2: 1.410(2); C2–C2a: 1.380(3); C2–N1:

1.403(2) Å). Therefore the dipyrido moiety of the ligand resembles more the *iso*- π -electronic heptafulvalene **IX** (bent) [18] or the similar dicycloheptapentalene **X** (planar) [19] (Fig. 4). The observed carbene angle of N1–C7–N1a (101.9(2)°) [20] is slightly smaller than found in other Cr(CO)₅(NHC) complexes [16].

The structure of the isomorphous tungsten complex **4** confirms the observations made for the chromium complex (**3a**). The C_{carbene}–W (2.261 Å), W–C_{trans} (1.979 Å) and C_{trans}–O (1.178 Å) bond lengths are in the typical ranges (C_{carbene}–W: 2.26–2.28; W–C_{trans}: 1.94–2.01; C_{trans}–O: 1.11–1.19 Å) for NHC tungsten pentacarbonyl complexes [7,13,21]. The alternating single and double bond lengths of the dipyrido moiety are found as well as a relatively small N1–C7–N1a angle of 102.6(4)°.

3. Summary and outlook

In conclusion we were able to synthesize the first metal complexes containing dipyridoimidazolynilidenes, which show an interesting structure with alternating single and double bonds. The strong high-field shift of the observed carbene ¹³C NMR signal indicates an electron rich carbene atom. Therefore modulation of the

Table 1
Crystal structure refinement for **3a** and **4**

	3a	4
Empirical formula	C ₁₆ H ₈ CrN ₂ O ₅	C ₁₆ H ₈ N ₂ O ₅ W
Formula weight	360.24	492.09
Temperature (K)	100(2)	200(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic
Space group	<i>Pbcn</i>	<i>Pbcn</i>
Z	4	4
Unit cell dimensions		
<i>a</i> (Å)	13.774(1)	14.0285(3)
<i>b</i> (Å)	14.903(1)	15.0622(2)
<i>c</i> (Å)	7.1621(7)	7.2347(1)
α (°)	90.0	90.0
β (°)	90.0	90.0
γ (°)	90.0	90.0
Volume (Å ³)	1470.2(2)	1528.69(4)
Density (calculated) (g/cm ³)	1.63	2.14
Absorption coefficient (mm ⁻¹)	0.81	7.59
Crystal colour/shape	Yellow/plate	Yellow/polyhedron
Theta range for data collection (°)	2.0–28.3	2.0–27.5
Index ranges	$-18 \leq h \leq 18, -19 \leq k \leq 19, -9 \leq l \leq 9$	$-18 \leq h \leq 18, -19 \leq k \leq 19, -9 \leq l \leq 9$
Reflections collected	14169	14644
Independent reflections (R_{int})	1829 (0.0384)	1762 (0.0341)
Observed reflections ($I > 2\sigma(I)$)	1514	1285
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.98 and 0.78	0.66 and 0.20
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	1829/0/127	1762/0/111
Goodness-of-fit on F^2	1.04	1.11
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.032, wR_2 = 0.074$	$R_1 = 0.020, wR_2 = 0.053$
Largest difference peak and hole (e Å ⁻³)	0.36 and -0.22	0.58 and -1.12

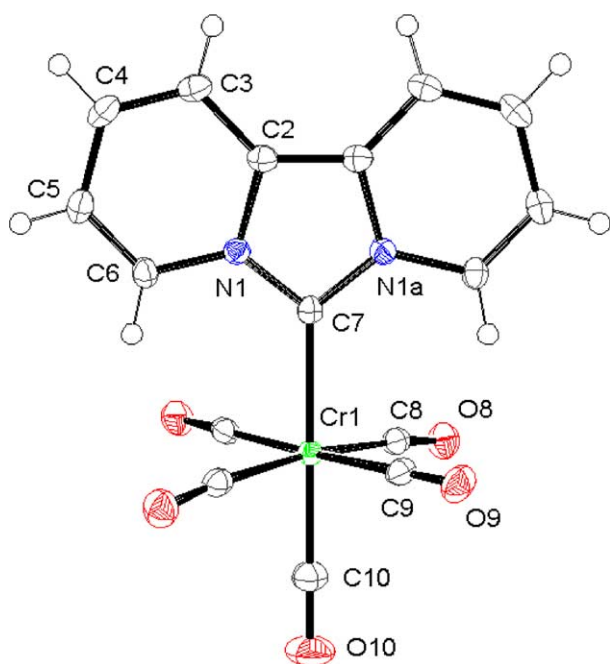


Fig. 3. ORTEP drawing of the structure of [Cr(CO)₅(dipyNHC)] (**3a**).

electronic structure of this carbene type with its conjugated π -system should be possible and is currently under investigation.

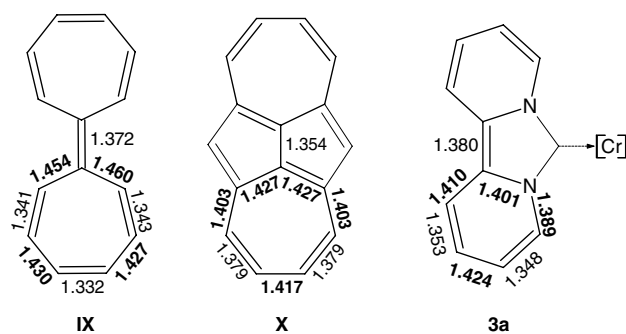


Fig. 4. The dipyrido moiety of the carbene ligand in **3a** shows similar bond lengths as found in the *iso*- π -electronic heptafulvalene **IX** or dicycloheptapentalene **X**.

4. Experimental

4.1. General comments

Unless otherwise noted all reactions were carried out under an atmosphere of dry argon using standard Schlenk techniques. Solvents were dried according to standard procedures and saturated with argon prior to use. Chemicals used were obtained from commercial suppliers and used without further purifications. The compound 2,2'-dipyrido[1,2-c;2',1'-e]imidazoliumiodide

(**1a**) and 4,4'-di-*tert*-butyl-2,2'-dipyrido[1,2-*c*;2',1'-*e*]imidazoliumiodide (**1b**) were synthesized according to the literature procedure [22]. Infrared spectra were recorded on a Bruker Equinox 55 FT-IR-spectrometer as a KBr pellet or in solution. UV/Vis spectra were measured on a Hewlett–Packard HP 8452 spectrometer. Mass spectra were recorded on a Jeol JMS-700 with NBA (nitrobenzylalcohol) or dichloromethane as matrix. Melting points were determined with a Büchi Melting Point B 540 apparatus. NMR spectra were recorded using a Bruker DRX 300 or DRX 500 spectrometer. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were calibrated to TMS on the basis of the relative chemical shift of the solvent as an internal standard. Elemental analyses were carried out at Mikroanalytisches Laboratorium der Chemischen Institute der Universität Heidelberg.

X-ray structural determinations: Frames corresponding to a sphere of data were collected using $0.3^\circ \omega$ scans with a SMART CCD area detector: radiation, Mo K α ; $\lambda = 0.71073 \text{ \AA}$. Intensities were corrected for Lorentz and polarization effects, and empirical absorption corrections were applied using the SADABS (V2.03) program [23] based on the Laue symmetry of the reciprocal space. Structure solutions and refinements were carried out with the SHELXTL (V6.12) program [24] system.

4.2. In situ generation of 2,2'-dipyrido[1,2-*c*;2',1'-*e*]imidazolin-7-ylidene (**2a**)

To 400 mg (1.36 mmol) of 2,2'-dipyrido[1,2-*c*;2',1'-*e*]imidazoliumiodide and 152 mg (1.36 mmol) sodium-*tert*-butanolate are added at -30°C 20 ml of tetrahydrofuran that were precooled to -30°C . After stirring for 30 min at -30°C the suspension is filtered off from sodiumchloride with a glass filter charged with Celite[®] and cooled to -30°C . The filtrate that contains the in situ generated carbene **2a** is ready for immediate use. ^1H NMR (THF- d_8 , -30°C): $\delta = 6.73$ – 6.85 (m, 4H, 4-H, 5-H) 7.85 (dt, $^3J_{\text{HH}} = 8.8 \text{ Hz}$, $^4J_{\text{HH}} = 1.3 \text{ Hz}$, 2H, 3-H), 8.48 (dt, $^3J_{\text{HH}} = 7.0 \text{ Hz}$, $^4J_{\text{HH}} = 1.24 \text{ Hz}$, 2H, 6-H). ^{13}C NMR (THF- d_8 , -30°C): $\delta = 115.5$, 118.9, 119.0 (C_{Ar}), 123.3 (C2), 130.3 (C_{Ar}), 197.8 ($\text{C7}_{\text{carbene}}$).

4.3. In situ generation of 4,4'-di-*tert*-butyl-2,2'-dipyrido[1,2-*c*;2',1'-*e*]imidazolin-7-ylidene (**2b**)

To 100 mg (0.24 mmol) of 4,4'-di-*tert*-butyl-2,2'-dipyrido[1,2-*c*;2',1'-*e*]imidazoliumiodide and 27.5 mg (0.25 mmol) potassium-*tert*-butoxide are cooled to -30°C and suspended in 8 ml of tetrahydrofuran which was precooled to -30°C . The reaction mixture is stirred for 30 min and filtered with a glass filter charged with Celite[®] and cooled to -30°C to remove sodiumiodide. The filtrate that contains the in situ generated carbene **2b** is ready for immediate use. ^1H NMR (THF- d_8 ,

-30°C): $\delta = 1.35$ (s, 18H, 9-H), 6.94 (dd, $^3J_{\text{HH}} = 7.6 \text{ Hz}$, $^4J_{\text{HH}} = 2.0 \text{ Hz}$, 2H, 5-H) 7.82 (m, 2H, 3-H), 8.44 (dd, $^3J_{\text{HH}} = 7.6 \text{ Hz}$, $^5J_{\text{HH}} = 1.0 \text{ Hz}$, 2H, 6-H). ^{13}C NMR (THF- d_8 , -30°C): $\delta = 30.8$ ($\text{C}(\text{CH}_3)_3$), 35.6 ($\text{C}(\text{CH}_3)_3$), 112.6 (C3), 115.0 (C5), 122.9 (C2), 129.8 (C6), 141.4 (C4), 196.3 ($\text{C}_{\text{carbene}}$).

4.4. Synthesis of chromium-2,2'-dipyrido[1,2-*c*;2',1'-*e*]imidazolin-7-ylidene-pentacarbonyl (**3a**)

440 mg (2.00 mmol) chromiumhexacarbonyl are photolysed in 60 ml of tetrahydrofuran for 5 h. The resulting orange solution is cooled to -30°C and the -30°C solution of the in situ generated carbene **2a** (1.36 mmol) is added dropwise. The reaction mixture is slowly warmed up to rt and stirred for 20 h. The solvent is removed in vacuo and excess chromiumhexacarbonyl removed by sublimation. The residue is washed 3 times with 5 ml each of methanol and dried in vacuo to give the product as a yellow solid. Yield: 64% (313 mg). ^1H NMR (THF- d_8): $\delta = 7.10$ – 7.16 (m, 2H, 4-H), 7.21– 7.27 (m, 2H, 5-H), 8.17 (dt, $^3J_{\text{HH}} = 8.9 \text{ Hz}$, $^4J_{\text{HH}} = 1.2 \text{ Hz}$, 2H, 3-H), 8.93 (dt, $^3J_{\text{HH}} = 7.4 \text{ Hz}$, $^4J_{\text{HH}} = 0.9 \text{ Hz}$, 2H, 6-H). ^{13}C NMR (THF- d_8): $\delta = 118.2$ (C5), 119.2 (C3), 120.2 (C4), 126.5 (C2), 128.0 (C6), 170.8 ($\text{C}_{\text{carbene}}$), 218.9 (CO_{cis}), 222.7 (CO_{trans}). Mp: 175–179 $^\circ\text{C}$ (dec.). Anal. Calc. for $\text{C}_{16}\text{H}_8\text{N}_2\text{O}_5\text{Cr}$: C, 53.35; H, 2.24; N, 7.78. Found: C, 53.27; H, 2.50; N, 7.74. IR (KBr): $\nu = 1883.6$ (vs), 1898.6 (s), 1950.9 (s), 1970.1 (m), 2052.7 (m) cm^{-1} . MS-FAB: $m/z = 360.2$ [M^+], 332.2 [$\text{M}^+ - \text{CO}$]. MS-HR-FAB: m/z Calc.: 359.9839 [M^+]. Found: 359.9847; Calc.: 331.9889 [$\text{M}^+ - \text{CO}$]. Found: 331.9875. UV/Vis (acetonitrile, $c = 0.28 \text{ mmol l}^{-1}$): 409 nm ($A = 3.27$, $\epsilon = 11679 \text{ l mol}^{-1} \text{ cm}^{-1}$), 439 nm ($A = 2.08$, $\epsilon = 7429 \text{ l mol}^{-1} \text{ cm}^{-1}$), 474 nm ($A = 0.89$, $\epsilon = 3179 \text{ l mol}^{-1} \text{ cm}^{-1}$).

4.5. Synthesis of chromium-4,4'-di-*tert*-butyl-2,2'-dipyrido[1,2-*c*;2',1'-*e*]imidazolin-7-ylidenepentacarbonyl (**3b**)

79.0 mg (0.360 mmol) of chromiumhexacarbonyl are suspended in 30 ml tetrahydrofuran and irradiated with UV-light for 5 h at room temperature. The solution is then cooled to -30°C and the freshly prepared solution of carbene **2b** in tetrahydrofuran added dropwise. The combined reaction mixtures are slowly warmed up to room temperature and stirred for 20 h. The solvent is removed under reduced pressure and residual chromiumhexacarbonyl sublimed off from the orange residue at 10^{-3} mbar and 35°C . After washing with 1 ml pentane and 3 times each with 5 ml of methanol and drying in vacuo the product can be isolated as a yellow solid. Yield: 60.0 mg (52%). ^1H NMR (CD_2Cl_2): $\delta = 1.40$ (s, 18H, 9-H), 7.16 (dd, $^3J_{\text{HH}} = 7.8 \text{ Hz}$, $^4J_{\text{HH}} = 2.0 \text{ Hz}$, 2H, 5-H), 7.77 (dd, $^4J_{\text{HH}} = 2.0 \text{ Hz}$, $^5J_{\text{HH}} = 0.9 \text{ Hz}$, 2H,

3-H), 8.70 (dd, $^3J_{\text{HH}} = 7.8$ Hz, $^5J_{\text{HH}} = 0.9$ Hz, 2H, 6-H). ^{13}C NMR (CD_2Cl_2): $\delta = 30.4$ (C9), 35.0 (C8), 112.0 (C3), 116.8 (C5), 125.1 (C2), 126.7 (C6), 142.3 (C4), 167.6 ($\text{C}_{\text{carbene}}$), 218.3 (C_{cis}), 222.4 (C_{trans}). Mp: 173–175 °C (dec.). Anal. Calc. for $\text{C}_{24}\text{H}_{24}\text{N}_2\text{O}_5\text{Cr} \cdot 0.3\text{-MeOH}$: C, 60.54; H, 5.27; N, 5.81. Found: C, 60.33; H, 5.19; N, 5.80. IR (KBr): $\nu = 1883.9$ (vs), 1899.8 (vs), 1949.7 (s), 1970.5 (m), 2052.7 (m) cm^{-1} . IR (CD_2Cl_2) $\nu = 1924.1$ (vs), 2054.2 (w) cm^{-1} ; (*n*-hexane) $\nu = 1927$ (vs), 2055 (w) cm^{-1} . MS-FAB: $m/z = 472.37$ [M^+], 444.38 [$\text{M}^+ - \text{CO}$]. MS-HR-FAB: m/z Calc.: 472.1091 [M^+]. Found: 472.1095.

4.6. Synthesis of tungsten-2,2'-dipyrido[1,2-*c*;2',1'-*e*]-imidazolin-7-ylidene-pentacarbonyl (**4**)

176 mg (500 μmol) tungstenhexacarbonyl are photolysed in 20 ml of tetrahydrofuran for 5 h. The resulting orange solution is cooled to -30 °C and the -30 °C solution of the carbene **2a** (generated in situ from 100 mg 340 μmol **1a** and 38.0 mg KO^tBu in 5 ml tetrahydrofuran) is added dropwise. The reaction mixture is slowly warmed up to rt and stirred for 20 h. The solvent is removed in vacuo and excess tungstenhexacarbonyl removed by sublimation. The residue is dissolved in tetrahydrofuran, covered with pentane and kept at 4 °C to give yellow crystals of the product that are collected by filtration and dried in vacuo. Yield: 49% (82.0 mg). ^1H NMR (THF-d_8): $\delta = 7.15$ – 7.18 (m, 2H, 4-H), 7.26– 7.29 (m, 2H, 5-H), 8.17 (d, $^3J_{\text{HH}} = 8.7$ Hz, 2H, 3-H), 8.92 (d, $^3J_{\text{HH}} = 7.4$ Hz, 2H, 6-H). ^{13}C NMR (THF-d_8): $\delta = 118.5$ (C5), 119.2 (C3), 120.7 (C4), 125.6 (C2), 129.7 (C6), 159.9 ($\text{C}_{\text{carbene}}$), 198.9 (CO_{cis}), 202.0 (CO_{trans}). Mp: 238–245 °C (dec.). Anal. Calc. for $\text{C}_{16}\text{H}_8\text{N}_2\text{O}_5\text{W}$: C, 39.05; H, 1.64; N, 5.69. Found: C, 40.27; H, 1.94; N, 5.87. IR (KBr): $\nu = 1881.1$ (vs), 1898.5 (s), 1946.9 (m), 2059.5 (w) cm^{-1} . MS-FAB+: $m/z = 492.24$ [M^+], 436.22 [$\text{M}^+ - \text{CO}$] (both tungsten isotope pattern). MS-HR-FAB+: $m/z =$ Calc.: 489.9890 [M^+] ^{182}W). Found: 489.9903; Calc.: 491.9943 [M^+] ^{184}W . Found: 491.9993; Calc.: 493.9977 [M^+] ^{186}W . Found: 494.0021. UV/Vis: (acetonitrile, $c = 0.2$ mmol l^{-1}): 310 nm ($A = 3.13$, $\epsilon = 15650$ $\text{l mol}^{-1} \text{cm}^{-1}$), 397 nm ($A = 2.54$, $\epsilon = 12700$ $\text{l mol}^{-1} \text{cm}^{-1}$), 441 nm ($A = 0.78$, $\epsilon = 3900$ $\text{l mol}^{-1} \text{cm}^{-1}$).

5. Supporting information available

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC 271513 (**3a**) and CCDC 271514 (**4**). Copies of these data can be obtained free of charge on request to The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK, fax: +44

1223 366 033, e-mail: deposit@ccdc.ac.uk or via www.ccdc.cam.ac.uk/conts/retrieving.html.

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