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Tungsten(0)-carbonyl complexes of naphthylazoimidazoles

Papia Datta^a, Ashis Kumar Patra^b, Chittaranjan Sinha^{a,*}

^a Department of Chemistry, Inorganic Chemistry Section, Jadavpur University, Kolkata, West Bengal 700 032, India
^b Inorganic and Physical Chemistry Department, Indian Institute of Science, Bangalore, India

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ABSTRACT

The reaction of W(CO)₆ with 1-alkyl-2-(naphthyl- α -azo)imidazole (α -NaiR) has synthesized [W(CO)₅(α -NaiR-N)] (α -NaiR-N refers to the monodentate imidazole-N donor ligand) at room temperature. The structure of [W(CO)₅(α -NaiMe-N)] shows a monodentate imidazole-N coordination of 1-methyl-2-(naphthyl- α -azo)imidazole (α -NaiMe). The complexes are characterized by elemental, mass and other spectroscopic data (IR, UV–Vis, NMR). On refluxing in THF at 323 K, [W(CO)₅(α -NaiR-N)] undergoes decarbonylation to give [W(CO)₄(α -NaiR-N,N')] (α -NaiR-N,N' refers to the imidazole-N(N), azo-N(N') bidentate chelator). Cyclic voltammetry shows metal oxidation (W⁰/W¹) and ligand reductions (azo/ azo⁻, azo⁻/azo⁼). The redox and electronic properties are explained by theoretical calculations using an optimized geometry. DFT computation of [W(CO)₅(α -NaiMe-N)] suggests that the major contribution to the HOMO/HOMO – 1 come from W d-orbitals and the orbitals of CO. The LUMOs are occupied by α -NaiR. A TD-DFT calculation has ascribed that HOMO/HOMO – 1 \rightarrow LUMO is a mixture of metal-to-ligand and ligand-to-ligand charge transfer underlying the CO \rightarrow azoimine contribution. The complexes show emission spectra at room temperature. [W(CO)₄(α -NaiR-N,N')] shows a higher fluorescence quantum yield (ϕ = 0.05–0.07) than [W(CO)₅(α -NaiR-N)] (ϕ = 0.01–0.02).

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1. Introduction

Transition metal-polypyridine complexes are attractive due to their crucial role in catalyses, photophysics and photochemistry, electrochemistry, supramolecular properties, medicinal activity etc. [1-3]. Recent years have witnessed a great deal of interest in the synthesis of new ligands with a diimine group (-N=C-C=N-)[4,5] (in the framework of pyridine derivatives) or the design of isolectronic groups to the diimine function, such as the azoimine function, (-N=N-C=N-) [6-29] (Scheme 1). The azoimine function is capable of stabilizing low valent metal oxidation states [22-25]. Zero valent Group 6 metal carbonyls are also stabilized by the azoimine (-N=N-C=N-) function [30-40]. The N-heterocyclic azo molecules belong to the azoimine family and have been used to explore the chemistry of transition [6-25] and non-transition metals [26-29]. We have designed 1-alkyl-2-(naphthylazo)imidazole (2) a potential member of the azoimine family [41-43]. The present work is concerned with W(0)-carbonyl complexes of 1-alkyl-2-(naphthyl- α -azo)imidazoles (α -NaiR). The reaction of α -NaiR, with $W(CO)_6$ under ambient conditions (298 K) in the presence of Me₃NO has synthesized the penta-carbonyl complexes, [W(CO)₅(α-NaiR-N)] (**3**) (imidazole-N coordinated α-NaiR is abbreviated as α -NaiR-N). Penta-carbonyl Group 6 transition metal com-

E-mail address: c_r_sinha@yahoo.com (C. Sinha).

plexes are a source of Fischer carbene precursors in the studies of organic transformations [44–46], and are even used as diagnostic probes in the determination of nucleosides by measuring v_{CO} of the coordinated CO [47].

 $[W(CO)_4(\alpha-NaiR-N,N')]$ exhibit high intense fluorescence emissions while $[W(CO)_5(\alpha-NaiR-N)]$ are weak emitters. The free ligand is non-fluorescent. The complexes were characterized by different spectroscopic studies (IR, UV–Vis, Mass, NMR, fluorescence), and the electrochemical properties have been studied with cyclic voltammetry. One of the penta-carbonyl complexes, $[W(CO)_5(\alpha-NaiMe-N)]$, has been structurally confirmed by a single crystal X-ray diffraction study. Theoretical calculations (DFT and TD-DFT) using an optimized molecular system have been carried out to predict the electronic structure, the spectral, redox and photophysical properties.

2. Experimental

2.1. Materials and measurements

The 1-alkyl-2-(naphthyl- α -azo)imidazoles (α -NaiR, **2**; R = CH₃ (**a**), CH₂-CH₃ (**b**), CH₂Ph (**c**)) were prepared by the reported procedure [42]. W(CO)₆ and Me₃NO · 2H₂O were Sigma–Aldrich reagents. The reactions were carried out under an extremely dry oxygen free atmosphere under atmos bags (Sigma–Aldrich).



^{*} Corresponding author. Fax: +91 033 2413 7121.

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Scheme 1.

Me₃NO · 2H₂O was dehydrated at a controlled temperature under reduced pressure before use. THF and *n*-heptane were dried before use [48]. The solution spectral studies were carried out using spectroscopic grade solvents from Lancester, UK. Microanalyses (C, H and N) were performed using a Perkin Elmer 2400 CHN elemental analyzer. Spectroscopic measurements were carried out using the following instruments: UV-Vis spectra, Lambda 25 Perkin Elmer; IR spectra (KBr disk, 4000–450 cm⁻¹), RX-1 Perkin Elmer; ¹H NMR and ¹³C NMR spectra in CDCl₃, Bruker 300 MHz FT-NMR spectrometers in the presence of TMS as an internal standard. The emission was examined on a LS 55 Perkin Elmer spectrofluorimeter at room temperature (298 K) in benzene under degassed conditions. The FAB-MS was collected from a JEOL-AX 500. Electrochemical measurements were carried out with a computer controlled EG & G PARC VersaStat model 250 Electrochemical instrument using a Pt-disk working electrode, a Pt-wire auxiliary electrode and [n-Bu₄N|[ClO₄] supporting electrolyte under inert (dry N₂) environment at scan rate of 50 mV S⁻¹. The solution was IR compensated and the results were collected at 298 K. The reported results were referenced to SCE in CH₂Cl₂ and were uncorrected for junction potentials.

The fluorescence quantum yield of the complexes was determined using carbazole as a reference for $[W(CO)_5(\alpha-NaiR-N)]$ (**3**) with a known ϕ_R value of 0.42 in C₆H₆ [49] and anthracene (ϕ_R of 0.62 in C₆H₆ [50]) as a reference for $[W(CO)_4(\alpha-NaiR-N,N')]$ (**4**). The complex and the reference dye were excited at the same wavelength, maintaining nearly equal absorbance (~0.1), and the emission spectra were recorded. The areas of the emission spectra were integrated using the software available in the instrument and the quantum yield was calculated according to the following equation:

$$\phi_{\rm S}/\phi_{\rm R} = [A_{\rm S}/A_{\rm R}] \times [(Abs)_{\rm R}/(Abs)_{\rm S}] \times [\eta_{\rm S}^2/\eta_{\rm R}^2]$$

here, ϕ_S and ϕ_R are the fluorescence quantum yields of the sample and reference, respectively. A_S and A_R are the areas under the fluorescence spectra of the sample and the reference respectively, $(Abs)_S$ and $(Abs)_R$ are the respective optical densities of the sample and the reference solution at the wavelength of excitation, and η_S and η_R are the values of refractive index for the respective solvents used for the sample and reference.

2.1.1. Preparation of W(CO)₅(α-NaiMe-N) (**3a**)

To W(CO)₆ (50 mg, 0.142 mmol) dissolved in dry THF (10 ml) was added Me₃NO (11 mg, 0.145 mmol), and the solution was stirred for 1 h. To the resulting yellow solution, α -NaiMe (34 mg, 0.144 mmol) was added and the solution was stirred for 6 h. The color of the solution changed to brown-red. The solvent was evaporated under reduced pressure and the crude product was passed down a neutral Al₂O₃ column. A brown-red solution was eluted

with benzene:pet-ether (60–80 °C) (1:1 v/v), followed by a small volume of a violet solution in the same solvent as a tailing band and this was rejected due to the negligibly small amount of the compound. Removal of the solvent of the brown-red solution afforded the analytically pure product (**3a**) in 45% yield.

Microanalytical data are as follows: Anal. Calc. for $[W(CO)_5(\alpha -$ NaiMe-N)] (**3a**), C₁₉H₁₂N₄O₅W: C, 40.71; H, 2.44; N, 10.00. Found: C, 40.66; H, 2.50; N, 10.10%. FAB-MS, M⁺ 560, (M-5CO)⁺ 420; IR (KBr, cm⁻¹) v_{CO} : 2068, 2015, 1916, 1881; IR in DCM v_{CO} : 2071, 2023, 1922, 1885; UV (λ_{max} , nm (ϵ , 10³ M⁻¹ cm⁻¹), benzene): 546 (2.045), 401 (4.696), 343 (3.768) (shoulder). Anal. Calc. for $[W(CO)_5(\alpha-NaiEt-N)]$ (3b), $C_{20}H_{14}N_4O_5W$: C, 41.81; H, 2.44; N, 9.76. Found: C, 42.00; H, 2.50; N, 9.64%. FAB-MS, M⁺ 574, (M-5CO)⁺ 434; IR (KBr, cm⁻¹) v_{CO} : 2068, 2015, 1907, 1853; IR in DCM v_{CO} : 2070, 2020, 1925, 1860; UV (λ_{max} , nm (ϵ , 10³ M⁻¹ cm⁻¹), benzene) 547 (3.822), 403 (15.328), 341 (8.547) (shoulder). Anal. Calc. for $[W(CO)_5(\alpha-NaiBz-N)]$ (3c), $C_{25}H_{16}N_4O_5W$: C, 40.17; H, 2.52; N, 8.81. Found: C, 40.08; H, 2.48; N, 9.00%. FAB-MS, M⁺ 636, (M–5CO)⁺ 496; IR (KBr, cm⁻¹) v_{CO}: 2068, 2016, 1974, 1918; IR in DCM v_{CO}: 2075, 2022, 1985, 1924; UV (λ_{max}, nm (ε, 10³ M⁻¹ cm⁻¹), benzene) 548 (4.3), 402 (12.733), 341 (7.342) (shoulder).

2.1.2. Preparation of $W(CO)_4(\alpha$ -NaiMe-N,N') (4a)

To W(CO)₆ (50 mg, 0.142 mmol) dissolved in dry THF (10 ml) was added Me₃NO (11 mg, 0.145 mmol), and the solution was stirred and refluxed for 0.5 h. To the resulting solution, α -NaiMe (34 mg, 0.144 mmol) was added and the solution was stirred and refluxed for an additional 4 h. The color of the solution changed to brown-violet. Then the solvent was evaporated under reduced pressure and the crude product was passed down a neutral Al₂O₃ column. A small volume of a brown-red band was eluted by benzene:pet ether (60–80 °C) (1:1 v/v), and this was rejected due to the very small amount of the compound. A violet solution was then collected using benzene:pet-ether (60–80 °C) (3:1 v/v) as eluent. Removal of the solvent afforded the analytically pure product (**4a**) in 60% yield.

Microanalytical data are as follows: *Anal.* Calc. for [W(CO)₄(α-NaiMe-N,N')] (**4a**), C₁₈H₁₂N₄O₄W: C, 40.60; H, 2.26; N, 10.53. Found: C, 40.54; H, 2.35; N, 10.46%. FAB-MS, M⁺ 532, (M–4CO)⁺ 420; IR (KBr, cm⁻¹) v_{CO} : 2011, 1913, 1866; IR in DCM v_{CO} : 2019, 1919, 1872; UV (λ_{max} , nm (ε , 10³ M⁻¹ cm⁻¹), benzene) 551 (7.226), 401 (4.381), 337 (6.121). *Anal.* Calc. for [W(CO)₄(α-NaiEt-N,N')] (**4b**), C₁₉H₁₄N₄O₄W: C, 41.76; H, 2.56; N, 10.25. Found: C, 41.68; H, 2.60; N, 10.34%. FAB-MS, M⁺ 546, (M–4CO) ⁺ 434; IR (KBr, cm⁻¹) v_{CO} : 2014, 1915, 1868; IR in DCM v_{CO} : 2021, 1922, 1871; UV (λ_{max} , nm (ε , 10³ M⁻¹ cm⁻¹), benzene) 552 (4.767), 420 (1.908), 337 (3.808). *Anal.* Calc. for [W(CO)₄(α-NaiBz-N,N')] (**4c**), C₂₄H₁₆N₄O₄W: C, 47.37; H, 2.63; N, 9.21. Found: C, 47.43; H, 2.68; N, 9.18%. FAB-MS, M⁺ 608, (M–4CO) ⁺ 496; IR (KBr, cm⁻¹) ν_{CO} : 2010, 1907, 1850; IR in DCM ν_{CO} : 2017, 1917, 1861; UV (λ_{max} , nm (ϵ , 10³ M⁻¹ cm⁻¹), benzene) 552 (8.851), 420 (6.376), 337 (8.289).

2.2. Transformation of $[W(CO)_5(\alpha-NaiR-N)]$ (3) to $[W(CO)_4(\alpha-NaiR-N,N')]$ (4)

Preparation of $[W(CO)_4(\alpha-NaiMe-N,N')]$ (**4a**) from $[W(CO)_5(\alpha-NaiMe-N)]$ (**3a**) is detailed below. A THF solution of $[W(CO)_5(\alpha-NaiMe-N)]$ (100 mg in 15 ml THF) was heated at 60 °C for 2.5 h, which leads to the preparation of $[W(CO)_4(\alpha-NaiMe-N,N')]$. The solution is evaporated to dryness and violet crystalline compounds were then isolated by chromatographic purification, as stated before, and dried in a CaCl₂ (fused) desiccator. Yield: 73%. Microanalytical data support the chemical formula $[W(CO)_4(\alpha-NaiR-N,N')]$

2.3. Crystallographic data collection and refinement of $[W(CO)_5(\alpha-NaiMe-N)]$ (**3a**)

Crystals were grown by slow evaporation of a benzene solution of $[W(CO)_5(\alpha-NaiMe-N)]$ (**3a**). Crystal parameters and refined data are summarized in Table 1. The data of **3a** $(0.80 \times 0.15 \times 0.10 \text{ mm})$ were collected by a fine focus sealed tube at 293(2) K using a fine focus graphite monochromator Bruker Smart CCD Area Detector (Mo K α radiation, λ = 0.71073 Å). Unit cell parameters were determined from least-squares refinement of setting angles with 2θ in the range $3.86^\circ \le \theta \le 49.42^\circ$. Of 9331 collected data, 3368 with $I > 2\sigma$ (I) were used for the structure solution. The *hkl* range was $-9 \le h \le 9$, $-12 \le k \le 12$, $-14 \le l \le 14$. Reflection data were recorded using the ω -scan technique. Data were corrected for Lorentz polarization effects and for linear decay. Semi-empirical absorption corrections based on ψ -scans were applied. Data reduction was carried out using the Bruker SAINT program. The structure was solved by the direct method using SHELXS-97 [51] and successive difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were fixed geometrically and refined using the riding model. In the final difference Fourier map the residual minima and maxima (-0.735,0.308 e/Å³) were evaluated using SHELXL-97 [52].

2.4. Computational details

All computations were performed using GAUSSIANO3 (GO3) software [53]. The Becke's three-parameter hybrid exchange functional and the Lee-Yang-Parr non-local correlation function [54] (B3LYP) was used throughout the calculations. A LanL2DZ basis set [55] for W, 6–31G(d, p) for C, H, N and O atoms were used for all types of calculations. In all cases, vibrational frequencies were calculated to ensure that the optimized geometries represented local minima. We performed TD-DFT calculations of the

Table 1

Selected crystallographic data for [W(CO)₅(α -NaiMe-N)] (3a).

	[W(CO) ₅ (α-NaiMe)] (3a)
Formula	$C_{19}H_{12}N_4O_5W$
Crystal size (mm ³)	$0.80 \times 0.15 \times 0.10$
Formula weight (g M ⁻¹)	560.18
Crystal system	triclinic
Space group	ΡĪ
a (Å)	7.788(3)
<i>b</i> (Å)	10.656(4)
<i>c</i> (Å)	12.111(5)
α (°)	88.238(6)
β (°)	84.039(6)
γ (°)	82.139(6)
V (Å ³)	990.0(7)
Ζ	2
T (K)	293(2)
D_{calc} (Mg/m ³)	1.879
λ (Å) (Mo Kα)	0.71073
Absorption coefficient (m M^{-1})	5.872
Data/restraints/parameters	3368/0/262
Goodness-of-fit on F ²	1.086
$R (F_{\rm o})^{\rm a} \left[I > 2\sigma (I) \right]$	0.0187
$wR (F_{\rm o})^{\rm b} [I > 2\sigma (I)]$	0.0438
R [all data] (wR [all data])	0.0206 (0.0445)
Largest difference in peak and hole $(e/Å^{-3})$	0.308, -0.735

^a $R = \sum ||F_{o}| - |F_{c}|| / \sum |F_{o}|.$

^b $wR = \{\sum [w(F_0^2 - F_c^2)^2] / \sum [w(F_0^2)^2] \}^{1/2}; w = [\sigma^2(F_0)^2 + (0.0235P)^2 + 0.1361P]^{-1}, \text{ where } P = (F_0^2 + 2F_c^2)/3.$

low-lying excitation at the singlet optimized geometry. The excitation energies were calculated by the TD-DFT approach.

3. Results and discussion

3.1. Synthesis

1-Alkyl-2-(naphthyl-α-azo)imidazole (Scheme 1: α-NaiR, **2**; R = CH₃ (**a**), CH₂-CH₃ (**b**), CH₂Ph (**c**)), may serve as a monodentate imidazole-N ligand (abbreviated: α-NaiR-N) and as a bidentate chelating agent (abbreviated: α-NaiR-N,N; where N and N' refer to N(imidazole) and N(azo) donor centers, respectively). The reaction of α-NaiR with W(CO)₆ in the presence of Me₃NO resulted in the isolation of the penta-carbonyl [W(CO)₅(α-NaiR-N)] (**3**) at room temperature (298 K). The reaction between α-NaiR and W(CO)₆ at a higher temperature (323 K) yielded the tetra-carbonyl complex [W(CO)₄(α-NaiR-N,N')] (**4**). The complexes **3** may be converted into **4** by refluxing in a high boiling solvent like acetonitrile, THF and 2-methoxyethanol (Scheme 2). The composition of the complexes is supported by microanalytical and spectroscopic data. The structure of the penta-carbonyl complex has been confirmed by single crystal X-ray structure determination of [W(CO)₅(α-



Scheme 2. Preparation of penta-carbonyl and tetra-carbonyl azo-imidazole.



Fig. 1. The ORTEP view of the complex $[W(CO)_5(\alpha-NaiMe-N)]$ (3a) showing the atom labeling scheme with 50% probability thermal ellipsoids.

NaiMe-N)] (**3a**) (Fig. 1). We have attempted to crystallize $[W(CO)_4(\alpha-NaiR-N,N')]$ (**4**), but failed to get good quality diffracting crystals.

3.2. Molecular structure of $[W(CO)_5(\alpha-NaiMe-N)]$ (3a)

The X-ray structure of $[W(CO)_5(\alpha-NaiMe-N)]$ (**3a**) is shown in Fig. 1 and selected bond parameters are listed in Table 2. The molecule consists of a central W atom surrounded by six coordination centers and the arrangement is distorted octahedral [56–59]. The atomic arrangement involves the coordination of five CO ligands and the imidazole-N of a 1-methyl-2-(naphthyl- α -azo)imidazole ligand. The coordinated imidazole is inclined at an angle of 7.95° to the pendant naphthyl group. The W–N (imidazole) distance is 2.268(3) Å and the W–C(O) distances lie I the range 1.954–2.035 Å. The W–C(17) displays the shortest distance (1.954(4) Å) and this is due to the trans influence of the imidazole-N coordina-

tion to the central W atom. The four equatorial W–C(O) distances are within the range 2.028–2.035 Å. The *trans* C–W–C angles are slightly deviated from the ideal value (180°): C(18)–W(1)–C(15), 174.93(14)° and C(19)–W(1)–C(16), 178.63(14)°, while the other C–W–C angles are *cis*-angles and lie in the range 87.8 to 92.5° (see Table 3).

3.3. Spectroscopic characterization

3.3.1. FT-IR and mass spectra

FT-IR spectra were taken in both in solution (CH₂Cl₂) and in the solid phase (solid KBr). The spectra (Fig. 2) show three or four bands [60]. The solution spectra (CH_2Cl_2) show v(CO) at 5– 15 cm⁻¹ higher frequency than that of the KBr-phase data. The mean value of the CO frequencies, v(CO), in these cases is lower $(\Delta v(CO) = 15-25 \text{ cm}^{-1})$ than that of M(CO)₄(2-PAP) (2-PAP = 2-(phenylazo)pyridine) [30–37]. This supports weaker π -acidity of the naphthylazoimidazoles than that of phenylazopyridine. On comparing with the spectral pattern and frequency of the CO stretching of [W(CO)₅(PQ)] [56–57] (PQ = 2-(2'-pyridyl)quinoxaline) the present complexes are assigned to a penta-carbonyl complex with octahedral coordination where the ligand α -NaiR binds as a monodentate imidazole-N donor agent (α -NaiR-N). The v(N=N) and v(C=N) bands appear at 1360–1390 and 1660– 1620 cm⁻¹, respectively. The mass fragmentation by FAB-MS of the complexes support the expected fragmentation pattern of M⁺, $(M-CO)^+$, $(M-2CO)^+$, $(M-3CO)^+$ etc. for both types of complexes.

3.3.2. UV–Vis spectra and emission properties

Benzene solutions of $[W(CO)_5(\alpha-NaiR-N)]$ (**3**) are brown-red and those of $[W(CO)_4(\alpha-NaiR-N,N')]$ (**4**) are brown-violet. The absorption spectra show three intense ($\varepsilon \sim 10^4$) bands within the region 330–600 nm (Fig. 3). The complexes do not show significant solvatochromism, unlike their Schiff base analogs [43]. In d⁶-octahedral complexes of the M(0)-state, the lowest energy electronic transition arises from a filled metal d-orbital to the unoccupied lowest energy π^* orbital of the ligand (MLCT). The transition at

Table 2

Selected bond lengths (Å) and angles (°) for the complex [W(CO)₅(α -NaiMe-N)] (3a) from the X-ray structure and theoretical calculated data by DFT for 3a and 4a.

Bond parameters	[W(CO) ₅ (α-NaiMe-N)] (3a)	[W(CO) ₄ (α-NaiMe-N,N')] (4a)			
	Experimental (e.s.d.)	Theoretical	Theoretical		
Bond lengths (Å)					
W(1)-N(1)	2.268(3)	2.258	2.143		
W(1)-C(15)	2.035(4)	2.036	a		
W(1)-C(16)	2.035(5)	2.035	2.049		
W(1)-C(17)	1.954(4)	1.989	1.997		
W(1)-C(18)	2.028(4)	2.036	2.034		
W(1)-C(19)	2.034(4)	2.040	1.968		
N(3)-N(4)	1.261(4)	1.301	1.338		
W(1)-N(4)	a	a	2.275		
Bond angles (°)					
C(15)-W(1)-N(1)	93.24(12)	89.72	a		
C(15)-W(1)-C(16)	88.22(16)	90.29	a		
C(16)-W(1)-N(1)	91.90(13)	89.58	103.12		
C(17)-W(1)-C(18)	87.45(15)	89.48	86.38		
C(17)-W(1)-C(19)	87.71(16)	90.17	84.44		
C(17)-W(1)-C(15)	87.81(15)	89.15	a		
C(17)-W(1)-C(16)	92.53(16)	89.82	82.23		
C(17)-W(1)-N(1)	175.48(11)	178.72	170.32		
C(18)-W(1)-C(19)	91.14(16)	89.04	89.77		
C(18)-W(1)-C(15)	174.93(14)	178.48	a		
C(18)- W(1)-C(16)	90.21(16)	90.37	170.23		
C(18)-W(1)-N(1)	91.62(13)	91.66	85.91		
C(19)-W(1)-C(15)	90.45(17)	90.30	a		
C(19)-W(1)-C(16)	178.63(14)	179.41	86.61		
C(19)–W(1)–N(1)	87.89(13)	90.44	89.66		

^a Because of the monodentate feature of α -NaiMe by the imidazole-N, the azo-N remains free.

Table 3¹H NMR spectral data of the complexes in CDCl₃.



Compound	δ (ppm) (J	δ (ppm) (J/Hz)								
	4-H ^a	5-H ^a	9-H ^c	10-11H ^d	12-14H ^d	15-Н ^с	N-CH ₃	N-CH ₂		
3a	7.50	7.02	8.65 (8.4)	8.12	7.63	7.98 (8.0)	4.10 ^b			
3b	7.57	7.17	8.64 (8.1)	8.06	7.70	7.80 (8.0)	1.59 ^e (7.5)	$4.50^{\rm f}(9.0)$		
3c ^g	7.60	7.21	8.66 (8.0)	8.15	7.74	7.83 (8.0)		5.64 ^b		
4a	7.66	7.4	8.13 (7.5)	7.91	7.47	7.82 (8.0)	4.01 ^b			
4b	7.45	7.20	8.17 (7.5)	7.93	7.50	7.82 (8.0)	1.57 ^e (7.5)	4.41 ^f (9.0)		
4c ^g	7.49	7.23	8.20 (7.5)	7.98	7.54	7.85 (8.0)		5.65		

^a Broad singlet.

^b Singlet.

^c Doublet.

d Multiplet.

e Triplet.

f Quartet.

^g δ [N–(CH₂)]–Ph:7.35–7.45 ppm.

545–555 nm of [W(CO)₅(α -NaiR-N)] (**3**) is assigned to a metal-toligand charge transfer transition [30–37,61,62]. In [W(CO)₄(α -NaiR-N,N')] (**4**) the bands in the visible region are shifted by \sim 10 nm to a longer wavelength region, which suggests a decrease in the energy gap between the d π (W)– π *(L) state. Other transitions at \sim 400 nm and \sim 340 nm may be attributed to intraligand (n– π */ π – π *) transitions (LLCT or ILCT). DFT and TD-DFT calcula-



Fig. 2. Solution FT-IR spectra in CH₂Cl₂.

tions of these complexes have undertaken to verify the electronic structure of the molecules, and they are discussed below.

The photoluminescence properties of the complexes (3 and 4)were studied at room temperature (298 K) in benzene (Fig. 3). The ligands are photo-inactive. The lowest singlet $S_0 \rightarrow S_1$ transition in the UV region (<400 nm) is in good agreement with the $\pi \cdot \pi^*$ transition. Longer wavelength excitation shows very weak emission. The excitation spectra are perfectly matched with the absorption spectra, which indicate sufficient stability of the excited state upon irradiation and this being structurally rigid against any chemical deformation at least on the spectroscopic timescale. The photophysics of these complexes shows high energy (HE) and low energy (LE) transitions. The low energy emission appears at 615-647 nm and its quantum yield has not been evaluated because of very low intensity. The quantum yields (ϕ) of the excitation at 331–341 nm (Table 4) show a better prospect for $[W(CO)_4(\alpha -$ NaiR-N,N')] (**4**) ($\phi = 0.05-0.07$) than [W(CO)₅(α -NaiR-N)] (**3**) (ϕ = 0.01-0.02). In the absence of a metal ion, the fluorescence of the ligand is probably deactivated through $n-\pi^*$ states rather than by PET (photoinduced electron transfer) [63].

Lifetime data of the complexes were taken in benzene solution when excited at 370 nm. The fluorescence decay curve was deconvoluted with respect to the lamp profile. The observed florescence decay fits with the bi-exponential nature of the complexes (Fig. 4). We have used the mean fluorescence lifetime ($\tau_f = a_1\tau_1 + a_2\tau_2$ where a_1 and a_2 are the relative amplitudes of the decay process) to compare the excited state (population at S₁ and S₂ states) stability of the complexes. The radiative and non-radiative rate constants (k_r and k_{nr}) are calculated and data show the usual higher k_{nr} value than the k_r value. The excited state is appreciably stable for [W(CO)₄(α -NaiR-N,N')] (**4**). We could not evaluate quantitative



Fig. 3. Absorption spectra of $[W(CO)_5(\alpha-NaiEt-N)](---)$, $[W(CO)_4(\alpha-NaiEt-N,N')](----)$ and fluorescence spectra of $[W(CO)_5(\alpha-NaiEt-N)](.....)$, $[W(CO)_4(\alpha-NaiEt-N,N')](----)$ in benzene. Higher energy emissions are recorded at 341 and 337 nm for **3b** and **4b**, respectively, and the lower energy emission is recorded at 552 nm wavelength for **4b**, shown in the inset figure.

Table 4

Cyclic voltammetry^a, fluorescence spectra^b and lifetime data.^c

Compound	Cyclic voltammetric data ^a			λ _{ex}	λ _{em}	Quantum	$\tau_{\rm f} ({\rm ns})^{\rm d}$	χ^2	$k_{ m r} imes 10^{-9}$	$k_{\rm nr} imes 10^{-9}$
	E (ligand), V ($\Delta E_{\rm p}$, mV)		E (metal), V ($\Delta E_{\rm p}$, mV)	(nm) ^b	(nm) ^b	yield (ϕ)			(s^{-1})	(s^{-1})
	Azo/azo ⁻	Azo ⁻ /azo ⁼	M^0/M^{+1}							
[W(CO) ₅ (α-NaiMe-N)] (3a)	-0.70 (120)	-1.28 (132)	0.982 (210)	343 (546)	383 (647)	0.0148	е	е	е	е
[W(CO) ₅ (α-NaiEt-N)] (3b)	-0.99 (110)	-1.40 (170)	1.04 (230)	341 (550)	385 (622)	0.0154	e	e	e	e
$[W(CO)_5(\alpha-NaiBz-N)]$ (3c)	-0.78 (120)	-1.33 (160)	1.021 (200)	341 (548)	383 (633)	0.0162	e	е	e	e
$[W(CO)_4(\alpha-NaiMe-N,N')]$ (4a)	-0.88 (120)	-1.37 (145)	0.712 (130)	337 (551)	391 (615)	0.0534	4.671	1.16	0.0032	0.2109
[W(CO) ₄ (α-NaiEt-N,N')] (4b)	-0.65 (120)	-1.14 (140)	0.718 (110)	337 (552)	397 (635)	0.0732	1.457	1.12	0.0503	0.6362
$[W(CO)_4(\alpha-NaiBz-N,N')] (4c)$	-0.70 (120)	-1.45 (170)	0.814 (125)	337 (550)	393 (634)	0.0601	0.987	1.18	0.0164	0.9965

^a Solvent, CH₂Cl₂; Pt-working electrode, SCE reference, Pt-auxiliary electrode; [*n*-Bu₄N](ClO₄) supporting electrolyte, scan rate 50 mV/s; metal oxidation E = 0.5 ($E_{pa} + E_{pc}$), V for M^{I}/M^{0} couple, $\Delta E_{p} = |E_{pa} - E_{pc}|$, mV; where E_{pa} (anodic-peak-potential) and E_{pc} (cathodic-peak-potential).

^b Solvent C₆H₆, second excitation and emission wavelength are given in brackets.

^c In C₆H₆ at 298 K.

^d Excitation at 370 nm.

^e $\tau_{\rm f}$, χ^2 , $k_{\rm r}$ and $k_{\rm nr}$ are not determined for these complexes because of very low emissions.

emission parameters of $[W(CO)_5(\alpha-NaiR-N)]$ (**3**). The presence of a dangling non-coordinated naphthylazo motive may be responsible for vibrational relaxation and energy transfer from the excited state that quenches the respective excited state. The emission features of these complexes may arise from the participation of π -acidic, strong field ancillary CO [64,65] with the third-row metal, which also increases the metal–ligand bonding [66–68]. The biexponential feature of the fluorescence decay may be due to population of the S₂ state in addition to the usual S₁ population.

3.4. Electrochemistry

The cyclic voltammetry of the compounds show one oxidation and two reductions. By analogy with similar types of α -diimine complexes, $[M(CO)_n(L)]$ (L = diimine or azoimine) [30–40] we advocate that the oxidation is primarily metal-centered. In the case of the tetra-carbonyl complexes (**4**), the oxidation on scan reversal shows a cathodic peak at a potential difference >100 mV to that of the anodic peak and supports quasireversibility (Fig. 5) of the voltammogram, while the penta-carbonyls (**3**) show irreversible oxidation. The results are collected in Table 4. Significantly $[W(CO)_5(\alpha$ -NaiR-N)] shows a higher potential than $[W(CO)_4(\alpha$ - NaiR-N,N'] by 0.2–0.3 V. This is obviously due to the presence of the strongly π -acidic additional CO group in complexes **3** compared to **4**. The reduction is referred to azo/azo⁻ and azo⁻/azo⁻, which appear at a more negative potential than those of the analogous 2-(phenylazo) pyridine complexes [30–37]. This is due to higher π -acidity of pyridine rather than imidazole and the electronic influx of the naphthyl rather than the phenyl group to the azo function.

3.5. DFT and TD-DFT calculations of $[W(CO)_5(\alpha-NaiMe-N)]$ and $[W(CO)_4(\alpha-NaiMe-N,N')]$

DFT and TD-DFT computations of optimized structures of $[W(CO)_5(\alpha-NaiMe-N)]$ (**3a**) and $[W(CO)_4(\alpha-NaiMe-N,N')]$ (**4a**) were performed to establish their electronic structure, spectral transitions and redox properties. The calculation has overthrown the earlier concept of MLCT transitions [66–70]. The structural agreement between theory and experiment is satisfactory (Table 2) for $[W(CO)_5(\alpha-NaiMe-N)]$. The theoretical W–N(1) length is 0.01 Å shorter than the observed one, while the W–C(17) bond *trans* to W–N(1) is elongated by ~0.03 Å compared to the experimental results. Other W–C distances are comparable, as are the angles (Table



Fig. 4. Bi-exponential decay profile (\odot) and fitting curve (-) of [W(CO)₄(α -NaiBz-N,N')] (**4c**) in benzene. Excitation is carried out at 370 nm.

2). The orbital energies, along with contributions from the ligands and metal, are given in the Supplementary Table. A correlation of MOs is given in Fig. 6. An interesting feature of the valence orbitals in $[W(CO)_5(\alpha-NaiMe-N)]$ is that the two highest occupied MOs (HOMO, abbreviated as H; HOMO – 1, abbreviated as H-1) are very close in energy (the difference is only 0.11 eV), with a significant contribution from the metal d-orbitals and the π^* orbital of the carbonyls. The contribution from COs is 30-40% while W contributes 50–60%. The two occupied MOs in $[W(CO)_4(\alpha-NaiMe-N,N')]$ (4a) H and H-1 are separated by 0.7 eV, while H-1 and H-2 are closely associated (the energy difference is only 0.17 eV). The LUMOs (L + n) are primarily π^* of the COs and α -NaiMe. The L (LUMO) and L + 2 (LUMO + 2) are mainly composed of α -NaiMe (L 99% α -NaiMe; L + 2 78% α -NaiMe) while L + 1, L + 3, L + 5 have >70% π^* of the COs. Although there is a substantial energy difference (\sim 1.6 eV) between L and L + 1, higher unoccupied MOs (L + 2, L + 3, etc.) are closely spaced. The energy separation between the HOMO and LUMO is lower ($\Delta E = 1 \text{ eV}$) in [W(CO)₄(α -NaiMe-N,N')] (**4a**) than $[W(CO)_5(\alpha-NaiMe-N)]$ (**3a**) ($\Delta E = 2.27 \text{ eV}$). The bonding scheme has unequivocally suggested the existence of two fragments in the complexes, namely the electron donor group $W(CO)_n$ and the electron acceptor group α -NaiMe.

To gain detailed insight into the electronic transitions, the TD-DFT calculations were performed on two series of complexes, namely [W(CO)₅(α -NaiMe-N)] and [W(CO)₄(α -NaiMe-N,N')]. H and H-1 are localized on parts of the metal (55–60%) and CO (30–40%), and L carries 99% ligand character (Supplementary Tables). The transition 545–555 nm may be assigned to H/H-1 \rightarrow L



Fig. 6. Energy level correlation diagram in the gas phase.

because of the very small energy difference (0.11 eV) between H and H-1. Thus the transition may be defined as an admixture of MLCT and LLCT transitions, as suggested by Vlcek [70], contradicting the widely accepted MLCT concept. The H-2 \rightarrow L transition may be responsible for the broadening of the MLCT and LLCT bands. The transitions $H/H-1/H-2 \rightarrow L+2$ may also contribute in part to the MLCT and LLCT transitions. The back-bonding, $W \rightarrow CO$ transitions may be assigned to H/H-1/H-2 \rightarrow L + 1/L + 3 transitions, and those may be obstructed by the intraligand $\pi \rightarrow \pi^*$ transitions localized on the napthylazoimidazole ligand at 400-420 nm (Table 5). This is indeed observed. The electronic spectra of the complexes $([W(CO)_5(\alpha-NaiMe-N)]$ and $[W(CO)_4(\alpha-NaiMe-N,N')])$ show three main transition regions: 545-555, 400-420 and 320-345 nm. The intensity of these transitions has been assessed from the oscillator strength (f). From the calculations, the longest wavelength band appears at 691.5 (f, 0.095) which is assigned to $H \rightarrow L$, while other bands around the main transition of low oscillator strength, such as $H-1 \rightarrow L$, $H-2 \rightarrow L$, and $H-4 \rightarrow L$, are a combination of MLCT and LLCT transitions. A second band of high oscillator strength (f, 0.321) appears at 460.0 nm, which is also of MLCT origin and the transitions around this band come from $H/H-1/H-2 \rightarrow L+1$, H- $2 \rightarrow L + 4$, and are of MLCT and LLCT origin. The third recognized band is located at 334.9 nm (f, 0.164) which is a ligand centered



Fig. 5. Cyclic voltammograms of (a) $[W(CO)_5(\alpha-NaiEt-N)]$ (**3b**) and (b) $[W(CO)_4(\alpha-NaiEt-N,N')]$ (**4b**) in CH₂Cl₂ using a Pt-disk working electrode, SCE reference and $[n-Bu_4N][ClO_4]$ as the supporting electrolyte.

Table 5
Selected list of excitation energies of $[W(CO)_5(\alpha-NaiMe-N)]$ (3a) and $[W(CO)_4(\alpha-NaiMe-N,N')]$ (4a) in the gas phase.

Excited state	λ (nm) ($f \times 10^3$)	Transitions
[W(CO) ₅ (α-NaiMe-N)] (3a)		
2	691.5 (0.0952)	(85%) HOMO (H) \rightarrow LUMO (L) (MLCT)
4	519.7 (0.0082)	(72%) H-4 \rightarrow L (IL), (12%) H-2 \rightarrow L (MLCT)
5	460.0 (0.3214)	$(75\%) \text{ H-3} \rightarrow \text{L (IL)}$
6	414.4 (0.0113)	(82%) HOMO \rightarrow L + 1 (MLCT), (11%) H-2 \rightarrow L + 4 (MLCT)
7	406.3 (0.0094)	(76%) H-1 \rightarrow L + 1 (MLCT), (10%) H-2 \rightarrow L + 3 (MLCT)
10	374.2 (0.0463)	$(89\%) \text{ H-5} \rightarrow \text{L (IL)}$
13	360.1 (0.0067)	$[(38\%) \text{ H-1} \rightarrow \text{L} + 3, (33\%) \text{ H-1} \rightarrow \text{L} + 4, (21\%) \text{ HOMO} \rightarrow \text{L} + 4] (\text{MLCT})$
14	336.9 (0.0983)	(26%) H-6 \rightarrow L (IL), [(33\%) HOMO \rightarrow L + 5, (19\%) H-2->L + 3, (11\%) H \rightarrow L + 2] (MLCT)
15	334.9 (0.164)	(54%) H-6 \rightarrow L (IL), (22%) HOMO \rightarrow L + 5 (MLCT)
17	321.0 (0.0043)	$[(73\%) \text{ HOMO} \rightarrow \text{L} + 2, (11\%) \text{ HOMO} \rightarrow \text{L} + 5] (\text{MLCT})$
22	283.0 (0.0135)	(88%) HOMO \rightarrow L + 6 (MLCT)
27	273.4 (0.0582)	$[(69\%) H-4 \to L+1, (15\%) H-3 \to L+3] (IL)$
32	261.8 (0.0464)	$(47\%) \text{ H-7} \rightarrow \text{L (IL)}$
36	254.8 (0.0662)	(23%) H-3 \rightarrow L + 5 (IL), [(22\%) HOMO \rightarrow L + 7, (14\%) HOMO \rightarrow L + 8] (MLCT)
39	250 (0.00274)	$[(35\%) \text{ H-1} \rightarrow \text{L} + 7, (21\%) \text{ H-1} \rightarrow \text{L} + 8] (\text{MLCT})$
[W(CO)₄(α-NaiMe-N,N')] (4a)		
3	593.3 (0.239)	$[(59\%)$ H-2 \rightarrow L (12%) H-1 \rightarrow L $[(MLCT)$
4	463.8 (0.255)	(77%) H-3 \rightarrow LUMO(IL)
5	430.1 (0.0192)	(84%) HOMO \rightarrow L + 1 (MLCT)
8	387.7 (0.0187)	(54%) H-6 \rightarrow LUMO, (23%) H-4 \rightarrow LUMO] (IL)
11	372.6 (0.0084)	(38%) H-2 \rightarrow L + 3, (25%) H-1 \rightarrow L + 1, (13%) HOMO \rightarrow L + 2 $(MLCT)$
13	346.4 (0.0123)	(80%) H-5 → LUMO (IL)
14	334.4 (0.025)	(79%) H-1 \rightarrow L + 2 (MLCT)
15	318.2 (0.044)	(77%) H-2 \rightarrow L + 2 (MLCT)
18	292.2 (0.0269)	$[(26\%) \text{ H-1} \rightarrow \text{L} + 6, (13\%) \text{ HOMO} \rightarrow \text{L} + 5, (11\%) \text{ H-1} \rightarrow \text{L} + 4, (10\%) \text{ HOMO} \rightarrow \text{L} + 8](\text{MLCT})$
21	285.6 (0.0163)	$[(32\%)$ H-1 \rightarrow L + 4, (21%) H-1 \rightarrow L + 6, (18%) HOMO \rightarrow L + 8](MLCT)
23	278.9 (0.032)	(61%) H-2 \rightarrow L + 4(MLCT), (10%) H-3 \rightarrow L + 2(IL)
27	268.4 (0.0249)	$[(24\%) H-3 \rightarrow L+2, (23\%) H-7 \rightarrow LUMO](IL), H-2 \rightarrow L+6 (11\%) (MLCT)$
30	258.0 (0.0142)	$[(37\%) \text{ H-3} \rightarrow \text{L} + 4, (14\%) \text{ H-4} \rightarrow \text{L} + 2](\text{IL}), (13\%)\text{H-1} \rightarrow \text{L} + 7 (\text{MLCT})$
31	256.7 (0.0237)	(38%) H-1 \rightarrow L + 5, (23%) H-1 \rightarrow L + 7, (10%) H-2 \rightarrow L + 5](MLCT)
32	252.8 (0.0178)	[(28%) H-2 → L + 5, (10%) H-1 → L + 7](MLCT), (24%) H-8 → LUMO (IL)

MLCT: metal-to-ligand charge transfer; LLCT: ligand-to-ligand charge transfer; IL: intraligand charge transfer; H = HOMO; L = LUMO.

transition (H-6 \rightarrow L), and associated transitions are H \rightarrow L + 2/L + 5, H-2 \rightarrow L + 3 which are intra ligand charge transfer and MLCT transitions. High energy transitions appear at 250–280 nm, and those mainly are of intra-ligand charge transfer origin.

4. Conclusion

Tungsten(0)–carbonyl complexes of 1-alkyl-2-(naphthyl- α azo)imidazoles (α -NaiR) are described. The complexes $[W(CO)_5(\alpha-NaiR-N)]$ are obtained at room temperature (298 K), which on heating lose one CO ligand to synthesize $[W(CO)_4(\alpha -$ NaiR-N,N')]. In [W(CO)₄(α -NaiR-N,N')], α -NaiR-N,N' serve as a bidentate chelating agent and in $[W(CO)_5(\alpha-NaiR-N)] \alpha-NaiR-N$ act as a monodentate imidazole-N donor ligand. The structure of $[W(CO)_5(\alpha-NaiMe-N)]$ has been confirmed by a single crystal Xray diffraction study, where α -NaiMe exhibits a monodentate nature. The complexes show emission spectra at room temperature; $[W(CO)_4(\alpha-NaiR-N,N')]$ shows a higher quantum yield ($\phi = 0.05-$ 0.07) than $[W(CO)_5(\alpha-NaiR-N)]$ ($\phi = 0.01-0.02$). Cyclic voltammetry shows metal oxidation and ligand reductions. DFT calculations of $[W(CO)_5(\alpha-NaiMe-N)]$ and $[W(CO)_4(\alpha-NaiR-N,N')]$ explain the origin of the electronic spectra and redox activities. The HOMO/ $HOMO - 1 \rightarrow LUMO$ transition is assigned as a mixture of MLCT and LLCT transitions, underlying the $CO \rightarrow azoimine$ contribution as calculated by the TD-DFT method.

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Appendix A. Supplementary data

CCDC 645195 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http:// www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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References

- J. Reedijk, in: G. Willkinson, J.A. Mccleverty (Eds.), Comprehensive Coordination Chemistry, vol. 2, Pergamon, Oxford, UK, 1987.
- [2] G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Pergamon Press, New York, 1982.
- [3] F.A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry, 5th ed., Wiley, Intersciences, New York, 1994.
- [4] H.-F. Zhu, L. Li, T. Okamura, W. Zhao, W.-Y. Sun, N. Ueyama, Bull. Chem. Soc. Jpn. 76 (2003) 761.
- [5] L.A. Garcia-Escudero, D. Miguel, J.A. Turiel, J. Organomet. Chem. 691 (2006) 3434.
- [6] K. Kalyansundaram, Coord. Chem. Rev. 46 (1982) 159.
- [7] B.K. Ghosh, A. Chakravorty, Coord. Chem. Rev. 95 (1989) 239.
- [8] N. Bag, A. Pramanik, G.K. Lahiri, A. Chakravorty, Inorg. Chem. 31 (1992) 40.
- [9] S. Serroni, S. Campagna, F. Puntoriero, C.D. Pietro, N.D. Mcclenaghan, F. Loisean, Chem. Soc. Rev. 30 (2001) 367.
- [10] A.C.G. Hotze, H. Kooijman, A.L. Spek, J.G. Haasnoot, J. Reedijk, New J. Chem. 28 (2004) 565.
- [11] R.E. Shepherd, Coord. Chem. Rev. 247 (2002) 147.
- [12] M.J. Overett, J.R. Moss, Inorg. Chim. Acta 358 (2005) 1715.
- [13] C.K. Pal, S. Chattopadhyay, C. Sinha, D. Bandhyopadhyay, A. Chakravorty, Polyhedron 13 (1994) 999.
- [14] P.K. Santra, R. Roy, C. Sinha, Proc. Indian Acad. Sci. (Chem. Sci.) 112 (2000) 523.

- [15] B.K. Santra, P. Munshi, G. Das, P. Bharadwaj, G.K. Lahiri, Polyhedron 18 (1999) 617.
- [16] P.K. Santra, P. Byabratta, S. Chattopadhyay, L.R. Falvello, C. Sinha, Eur. J. Inorg. Chem. 1124 (2002).
- [17] M. Panda, S. Das, G. Mostafa, A. Castineiras, S. Goswami, J. Chem. Soc., Dalton Trans. (2005) 1249.
- [18] U.S. Ray, Sk. Jasimuddin, B.K. Ghosh, M. Monfort, J. Ribas, G. Mostafa, T.-H. Lu, C. Sinha, Eur. J. Inorg. Chem. (2004) 250.
- [19] U.S. Ray, B.G. Chand, G. Mostafa, J. Cheng, T.-H. Lu, C. Sinha, Polyhedron 22 (2003) 2587.
- [20] D. Banerjee, U.S. Ray, J.-C. Liou, C.-N. Lin, T.-H. Lu, C. Sinha, Inorg. Chim. Acta 358 (2005) 1019.
- [21] U.S. Ray, D. Banerjee, B.G. Chand, J. Cheng, T.-H. Lu, C. Sinha, J. Coord. Chem. 58 (2005) 1105.
- [22] T.K. Misra, D. Das, C. Sinha, P. Ghosh, C.K. Pal, Inorg. Chem. 37 (1998) 1672.
- [23] T.K. Misra, D. Das, C. Sinha, Polyhedron 16 (1997) 4163.
- [24] T.K. Misra, D. Das, C. Sinha, Indian J. Chem. 37A (1998) 741.
- [25] S. Pal, T.K. Misra, P. Chattopadhyay, C. Sinha, Proc. Indian Acad. Sci. (Chem. Sci.) 111 (1999) 687.
- [26] B.G. Chand, U.S. Ray, J. Cheng, T.-H. Lu, C. Sinha, Polyhedron 22 (2003) 1213.
- [27] B.G. Chand, U.S. Ray, G. Mostafa, T.-H. Lu, C. Sinha, Polyhedron 23 (2004) 1669.
- [28] B.G. Chand, U.S. Ray, G. Mostafa, T.-H. Lu, C. Sinha, J. Coord. Chem. 57 (2004) 627.
- [29] B.G. Chand, U.S. Ray, J. Cheng, T.-H. Lu, C. Sinha, Inorg. Chim. Acta 358 (2005) 1927.
- [30] M.N. Ackermann, C.R. Barton, C.J. Deodene, E.M. Specht, S.C. Keill, W.E. Schreiber, Hiodong Kim, Inorg. Chem. 28 (1989) 397.
- [31] F. Alper, C. Kayram, S. Ozkar, J. Organomet. Chem. 691 (2006) 2734.
- [32] W. Kaim, S. Ernst, S. Kohlmann, Polyhedron 5 (1986) 295.
- [33] W. Kaim, S. Kohlmann, Inorg. Chem. 25 (1986) 3442.
- [34] W. Kaim, S. Kohlmann, Inorg. Chem. 26 (1987) 68.
- [35] M.N. Ackermann, W.G. Fairbrother, N.S. Amin, C.J. Deodene, C.M. Lamborg, P.T. Martin, J. Organomet. Chem. 523 (1996) 145.
- [36] M.J. Alder, W.I. Cross, K.R. Flower, R.G. Pritchard, J. Organomet. Chem. 568 (1998) 279.
- [37] M.N. Ackermann, S.R. Kiihne, P.A. Saunders, C.E. Barnes, S.C. Stalling, H. Kim, C. Woods, M. Lagunoff, Inorg. Chim. Acta 334 (2002) 193.
- [38] M.N. Ackermann, M.P. Robinson, I.A. Maher, E.B. LeBlane, R.V. Raz, J. Organomet. Chem. 682 (2003) 248.
- [39] P. Datta, P. Gayen, C. Sinha, Polyhedron 25 (2006) 3435.
- [40] B.P. Buffin, P.J. Squattrito, A.O. Ojewole, Inorg. Chem. Commun. 7 (2004) 14.
- [41] J. Dinda, D. Das, P.K. Santra, C. Sinha, L.R. Falvello, J. Organomet. Chem. 629 (2001) 28.
- [42] S. Pal, D. Das, P. Chattopadhyay, C. Sinha, K. Panneerselvam, T.-H. Lu, Polyhedron 19 (2000) 1263.
- [43] P. Datta, C. Sinha, Polyhedron 26 (2007) 2433.

- [44] W. Palitzsch, U. Bohme, G. Roewer, Chem. Commun. (1997) 803.
- [45] M.M. Abd-Elzahar, T. Froneck, G. Roth, V. Gvozdev, H. Fischer, J. Organomet. Chem. 599 (2000) 288.
- [46] H. Fischer, J. Schmidt, J. Mol. Catal. 46 (1988) 277.
- [47] J.M.D.R. Toma, D.E. Bergstrom, J. Org. Chem. 59 (1994) 2418.
- [48] A.I. Vogel, A Text Book of Practical Organic Chemistry, Longman, London, 1959.
- [49] J.N. Deams, G.A. Crosby, J. Phys. Chem. 75 (1971) 991.
- [50] W.R. Dawson, M.W. Windsor, J. Phys. Chem. 72 (1968) 3251.
- [51] G.M. Sheldrick, SHELXS 97, Program for the Solution of Crystal Structure, University of Gottingen, Germany, 1990.
- [52] G.M. Sheldrick, SHEIXL 97, Program for the Refinement of Crystal Structure, University of Gottingen, Germany, 1997.
- [53] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T.A. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez, J.A. Pople, GAUSSIAN98, Gaussian Inc., Pittsburgh, PA, 1998.
- [54] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.
- [55] P.J. Hay, W.R. Wadt, J. Chem. Phys. 82 (1985) 270.
- [56] I. Veroni, C.A. Mitsopoulou, F.J. Lahoz, J. Organomet. Chem. 691 (2006) 5955.[57] I. Veroni, C. Makedonas, A. Rontoyianni, C.A. Mitsopoulou, J. Organomet. Chem.
- 691 (2006) 267. [58] J. Qin, R.L. Christopher, M.E. Edward, R. van Eldik, J. Phys. Chem. A 101 (1997)
- 243. [59] D.-B. Carlos, G. Friedrich-Wilhelm, R. van Eldik, Organometallics 17 (1998)
- 1669.
 [60] L. Rivera-Rivera, F. Colon-Padilla, A. Del Toro-Novales, J.E. Cortes-Figuerca, Synthesis (1998) 1534.
- [61] V.N. Nemykin, J.G. Olsen, E. Perera, P. Basu, Inorg. Chem. 45 (2006) 3557.
- [62] W.-F. Wu, R.Van. Eldik, Inorg. Chem. 37 (1998) 1044.
- [63] B. Valuer, Molecular Fluorescence: Principles and Applications, Wiley-VCH, Weinheim, 2001.
- [64] E.Y. Li, Y.-M. Cheng, C.-C. Hsu, P.-T. Chou, G.-H. Lee, I.-H. Lin, Y. Chi, C.-S. Liu, Inorg. Chem. 45 (2006) 8041.
- [65] P.A. Anderson, F.R. Keene, T.J. Meyer, J.A. Moss, G.F. Stouse, J.A. Treadway, J. Chem. Soc., Dalton Trans. (2002) 3820.
- [66] C.-L. Lee, R.R. Das, J.-J. Kim, Chem. Mater. 16 (2004) 4642.
- [67] M.K. Nazeemuddin, R. Humphry-Baker, D. Bermer, S. River, L. Zuppiroli, M. Graetzel, J. Am. Chem. Soc. 125 (2003) 8790.
- [68] A. Vlcek Jr., Coord. Chem. Rev. 230 (2002) 225.
- [69] S. Zalis, M. Burby, T. Kotrba, P. Maouses, M. Towrie, A. Vleck Jr., Inorg. Chem. 43 (2004) 1723.
- [70] I.R. Farrell, A. Vlcek, Coord. Chem. 208 (2000) 87.