Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Organometallic Chemistry 690 (2005) 168–176
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Dimethylplatinum (II) complexes with isocyanocoumarin ligands: the crystal structure of *cis*-dimethylbis-(7-diethylamino-3-isocyanocoumarin)platinum(II)

Craig Anderson [a,*], Daniel A. Freedman [b], Michael Jennings [c], Brenda Gray [a]

[a] *Department of Chemistry, Bard College, 30 Campus Road, Annandale-on-Hudson, NY 12504, USA*
[b] *Department of Chemistry, State University of New York at New Paltz, New Paltz, NY 12561, USA*
[c] *Department of Chemistry, University of Western Ontario, London, Ont., Canada N6A 5B7*

Received 29 June 2004; accepted 2 September 2004
Available online 7 October 2004

Abstract

Platinum complexes that contain isocyanocourmarin ligands have been prepared. $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ and $[PtPh_2(SMe_2)_2]$ react with ligands L, (L = 7-diethylamino-3-isocyanocoumarin, Idc; 7-isocyano-4-methylcoumarin, Mic; 7-isocyano-4-trifluoromethylcoumarin, Tic; 3-chloro-4-methyl-7-isocyanocoumarin, Cmic), to give PtR_2L_2, monomers in high yield. The NMR and IR spectra of these complexes are consistent with *cis* stereochemistry. The UV–Vis absorption spectra of the complexes show bands assigned to ligand-centered transitions. Excitation into the absorption bands of the Idc complexes gives emission at room temperature in methylene chloride solution. The oxidative addition reaction of two of these complexes with methyl iodide has been studied. Platinum (IV) species with *fac* geometry have been isolated and characterized. *Cis*-dimethylbis-(7-diethylamino-3-isocyanocoumarin)platinum(II) was characterized by X-ray diffraction.

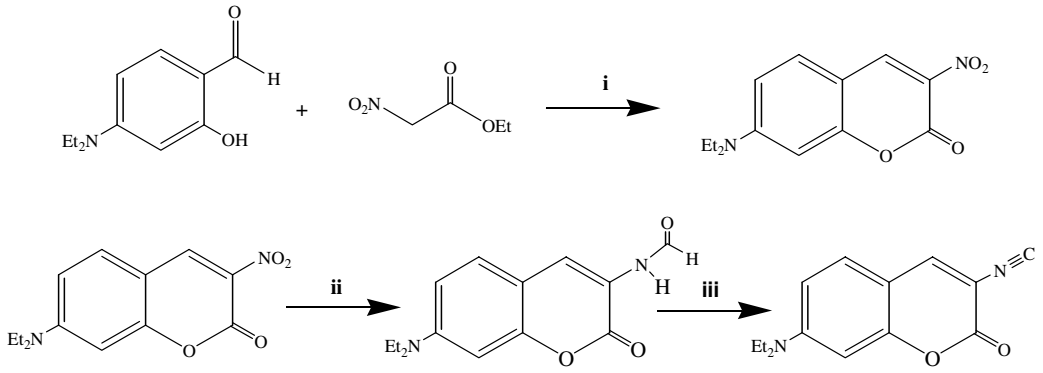
Keywords: Platinum; Oxidative addition; Photochemistry; Isocyanide; Coumarin

1. Introduction

Square-planar platinum (II) complexes with metal-to-ligand charge transfer (MLCT) excited states have been the subject of considerable interest due to their interesting photophysical properties, their potential applications as light emitting diodes, and as devices for solar energy conversion and hydrogen production [1]. The vast majority of these studies have focused on Pt(II) complexes of polypyridyl-type ligands. We thought it would be interesting to examine other Pt(II) complexes also likely to exhibit MLCT excited states. Therefore, in this work we describe the synthesis and characterization of a series of $R_2Pt(CNR)_2$ (R = Me, Ph) complexes where CNR is an isocyanocoumarin ligand (7-diethylamino-3-isocyanocoumarin, Idc; 7-isocyano-4-methylcoumarin, Mic; 7-isocyano-4-trifluoromethylcoumarin, Tic; 3-chloro-4-methyl-7-isocyanocoumarin, Cmic). The preparation of three of the isocyanocoumarin ligands and the $Mo(CO)_4L_2$ complexes of the ligands was recently reported [2]. The molybdenum complexes displayed intense visible absorption and emission bands that were assigned to MLCT transitions. The assignment was, in part, based on the similarities between the isocyanocoumarin complexes and analogous $Mo(pp)(CO)_4$ complexes (pp = polypyridyl) which have very well characterized emissive MLCT excited states [3]. It seems reasonable that MLCT excited states should also be observed for Pt–isocyanocoumarin complexes. We also report the preparation of a new isocyanocoumarin ligand, Idc, which differs from the other isocyano-

* Corresponding author. Tel.: +845 758 7293; fax: +845 758 7628.
E-mail address: canderso@bard.edu (C. Anderson).

0022-328X/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2004.09.007



Scheme 1. (i) Reflux in toluene with piperidine. (ii) Reflux with Sn in toluene/formic acid. (iii) Stir with $POCL_3/Net_3$ in CH_2Cl_2.

coumarin ligands in that it contains an intramolecular charge transfer (ICT) chromophore which generates intense visible absorption and emission bands. There is considerable evidence in the literature that platinum complexes with isocyanide ligands should be stable and display interesting properties. Recent reports on Pt(II)–isocyanide complexes have explored their liquid crystal properties [4], their use as probes for important intermediates in platinum catalyzed reactions [5], and their use as vapochromic sensors [6]. Coumarins and their derivatives [7] are of interest in natural products chemistry [8], have been shown to bond with DNA [9], and have exciting photochemical and photophysical properties of their own [10].

2. Preparation and characterization of 7-diethylamino-3-isocyanocoumarin (Idc)

Idc is easily prepared in the three steps shown in Scheme 1. Idc was fully characterized by elemental analysis, and by NMR, IR, UV–Vis, and emission spectroscopies. The absorbance spectrum (Fig. 1) in CH_2Cl_2 solution is dominated by an intense band at 420 nm. Also shown in Fig. 1 is the intense emission centered at 490 nm generated by excitation into the absorption band. Both the absorption and emission bands are consistent with what has been observed for other 7-aminocoumarin compounds [2]. The emissive excited state can be represented by the resonance structure on the right shown below (Fig. 2) where charge has been transferred from the amine to the unsaturated lactone ring.

3. Synthesis and characterization of the $PtR_2(CNR)_2$ complexes, R = Me or Ph

$Pt(CH_3)_2(CNR)_2$ complexes were readily prepared from $[Pt(CH_3)_2(\mu\text{-}SMe_2)]_2$ and $PtPh_2(CNR)_2$ complexes were prepared from $PtPh_2$ $(SMe_2)_2$ by displacement of the sulfide ligand with an isocyanocoumarin ligand (Chart 1) by mixing the appropriate ligand with the metal complex. Complexes were isolated in high yield as light yellow (Mic, Tic, Cmic complexes) or yellow-orange (Idc complexes) powders (Chart 1 and Reactions (1) and (2)).

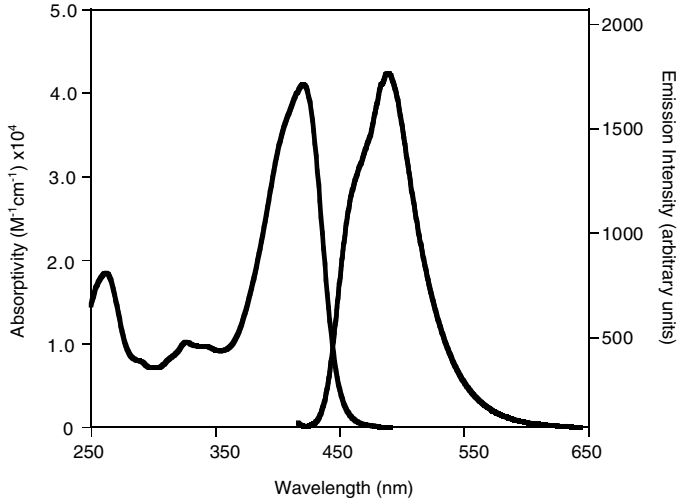


Fig. 1. Absorption and emission spectra of Idc in methylene chloride solution.

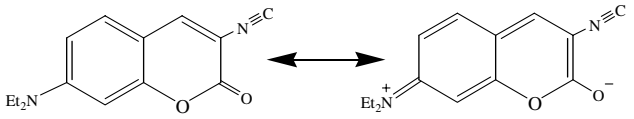
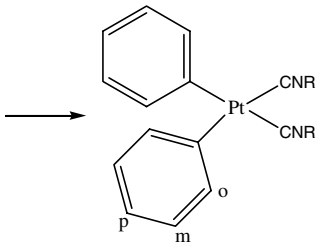


Fig. 2. Resonance structures for Idc.

$$[Pt(CH_3)_2(\mu\text{-}SMe_2)]_2 + 4CNR \rightarrow cis-[Pt(CH_3)_2(CNR)_2] \quad (1)$$

$$Ph_2Pt(SMe_2)_2 \quad + \quad 2\ CNR,\ CNR = Idc,\ Mic$$



(2)

The complexes were characterized by elemental analysis and IR, NMR, UV–Vis and emission spectroscopies.

The infrared spectra of the complexes display two isocyanide stretches, consistent with *cis* geometry. The proton NMR spectra of the complexes with R = Me shows one peak for the methyl ligands with platinum satellites with coupling constants of 74 Hz, consistent with the J_{Me-Pt} values for two other *cis*-dimethylplatinum(II)–isocyanide complexes already reported [11,12]. This indicates that the *trans* influence of the isocyanocoumarins ligands is similar to other isocyanide ligands and intermediate between bipy and phosphine ligands [13–17]. The geometry was confirmed by the crystal structure of the $[Pt(CH_3)_2(Idc)_2]$ (see below). The ^1H NMR peaks assigned to the isocyanocoumarin ligands are shifted slightly, but are otherwise nearly identical to the analogous peaks observed for the free ligands.

4. X-ray crystallography

X-ray quality crystals of $PtMe_2(Idc)_2$ were grown from a concentrated methylene chloride solution by slow diffusion of methanol. The crystal structure is composed of discrete molecules separated by van der Waals forces. A view of the molecule showing the labeling scheme is seen in Fig. 3. The molecule adopts a *cis* configuration as expected from the Pt precursor used and consistent with the IR and NMR data. Selected bond lengths and angles are given in Table 1.

Bond lengths in the coordination sphere of platinum are in the usual range and not significantly different than those reported for the similar complex, dimethylbis–(dimethylisocyanide)platinum (II) and are approximately the sum of the covalent radii for Pt (II) and sp^3 methyl [18]. The platinum carbon bond for the isocyanocoumarin ligand is slightly shorter than in a related complex, $Mo(CO)_4(Tic)_2$ [2], partially attributable to the CNR ligand being *trans* to methyl groups which are known to be stronger σ donors and weaker π acids than CO. Examination of the bond angles between adjacent atoms around the platinum (87°, 88°, 88° and 98°) shows the platinum center to be roughly square planar. The largest angle (98°) is between the coumarin rings as anticipated from a strictly steric consideration. A plane defined by the platinum atom and its four coordinated atoms has a mean deviation of 0.0305 Å. Both coumarin rings are twisted with respect to the platinum square plane. The C1–O13 coumarin is twisted 8.9° from the platinum square plane and the C21–O31 coumarin is twisted 32.4° from the platinum plane. Each coumarin ring forms loose stacks with the rings of adjacent molecules in a head-to-tail fashion. The C1–O13 coumarin ring completely eclipses itself, as does the C21–O31 coumarin ring. This full-eclipse puts the two coumarin rings at a perpendicular distance of 3.51(1) Å for C1–O13 and 3.52(1) Å for C21–O31. It is assumed that ππ interaction governs this contact distance. Thus the coumarin rings appear to pack in an orderly manner up the diagonal with the left "wing" eclipsing the "wing" below it and the right "wing" being eclipsed by the "wing" above it. There is some partial overlap of the coumarin rings as these extended, full-eclipse chains pack together. The C1–O13 manages to get within a perpendicular distance of 3.19(1) Å of itself. The C21–O31 stays further apart, 3.99(1) Å. Fig. 4 shows the two molecules in the unit cell that are in full-eclipse.

5. Oxidative addition study and platinum (IV) species

Dimethylplatinum(II) complexes are highly reactive towards oxidative addition [19,20]. In order to determine any effect that a change in oxidation state might have on the ligand-centered emission, the $PtMe_2(Idc)_2$ complex was reacted with methyl iodide to obtain a six-coordinate platinum (IV) complex. Reaction of $Pt(CH_3)_2(Idc)_2$ (reaction (3)) with an excess of methyl iodide

$$cis-[Pt(CH_3)_2(CNR)_2] + MeI \rightarrow fac\text{-}[Pt(CH_3)_3(CNR)_2I] \quad (3)$$

gave a yellow-orange solid. The reaction was complete within 24 h under the above conditions and can be approximated to be on the slower end of the range for similar dimethylplatinum complexes containing nitrogen ligands and comparable to *cis*-dimethylbis-(*o*-tolylisocyanide) [11,20]. It is generally accepted that oxidative addition of alkyl halides to platinum (II) compounds give *trans* stereochemistry, although *cis* isomers can be

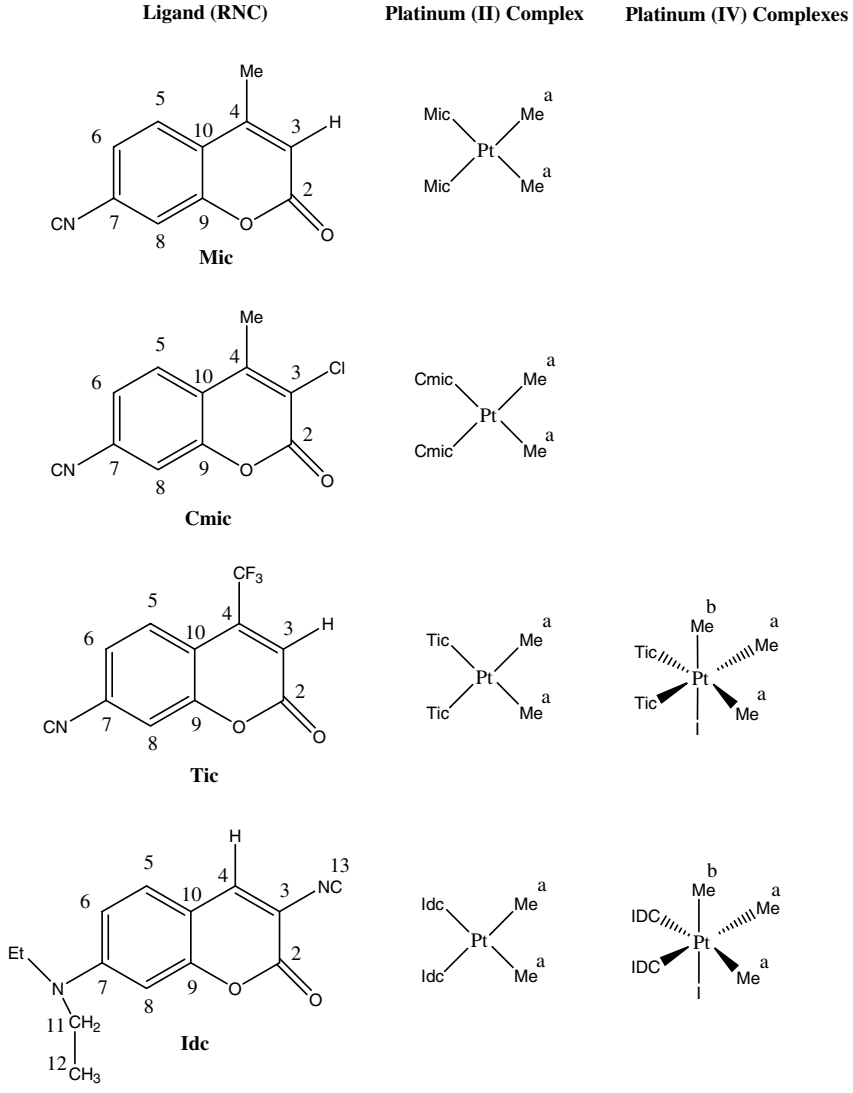


Chart 1.

produced by subsequent isomerization reactions [19]. The ^{1}H and ^{13}C NMR spectra are consistent with trans addition and no isomerization process to give a single product, *fac*-$[Pt(CH_3)_3(Idc)_2I]$. We also did not witness the formation of any carbene products that may have resulted by attack at the isocyanide or any polymeric or cationic species that have been reported for related complexes [21,22]. It appears that the complex, due to the two methyls groups, is electron-rich enough to give a single product, that of oxidative addition [11]. The *fac* geometry is the preferred geometry as it has no mutually *trans* carbon ligands which have a high trans influence and the values for platinum coupling constants for mutually trans methyls are much lower than those observed here (see below) [23]. The methylplatinum region of the proton NMR spectrum is very helpful in this assignment. Upon oxidative addition the peak for the two equivalent methyl groups of the platinum (II) species disappears and two new peaks in a 2:1 ratio appear shifted slightly upfield in comparison. The ^{2}J(Pt–H) coupling constant for the methyls *trans* to the isocyanocoumarin ligands (the greater ratio of the methyl peaks)

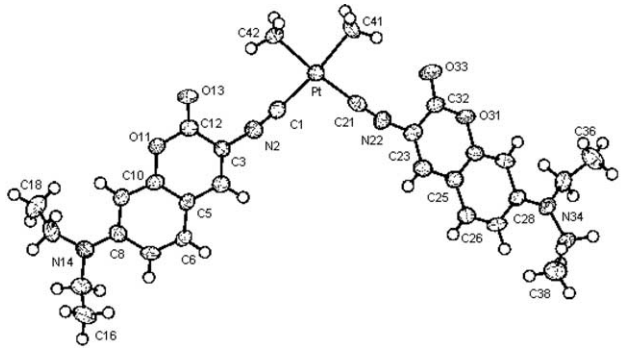


Fig. 3. Molecular structure of compound **3**.

Table 1
Selected bond lengths and bond angles in compound **3**

Bond lengths	
Pt–C(21)	1.955(8)
Pt–C(1)	1.971(7)
Pt–C(41)	2.084(6)
Pt–C(42)	2.087(7)
C(10)–N(2)	1.146(9)
N(2)–C(3)	1.385(9)
Bond angles	
C(21)–Pt–C(1)	98.6(3)
C(21)–Pt–C(41)	88.3(3)
C(1)–Pt–C(41)	172.8(3)
C(21)–Pt–C(42)	173.1(3)
C(1)–Pt–C(42)	86.3(3)
C(41)–Pt–C(42)	86.3(3)
C(1)–N(2)–C(3)	170.9(7)
N(2)–C(1)–Pt	174.6(6)

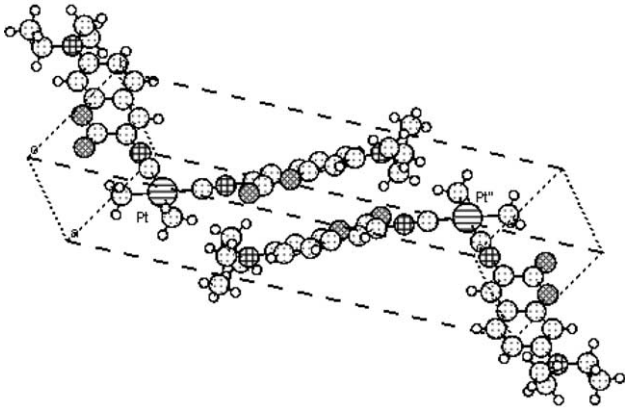


Fig. 4. Stacking of two molecules showing eclipsed coumarin rings.

decreases from 74 Hz in the platinum (II) complex to 63 Hz for the platinum (IV) complex as is expected and typical of oxidative addition products [20,23]. The methyl *trans* to iodide is assigned to the peak at higher field as it integrates to half the size of the other methyl peak and has a coupling constant of 71 Hz. The coupling constant, which is greater than that of the other methyl peak, is expected due to iodine having a weaker *trans* influence than isocyanide. The carbon-13 NMR shows the same pattern for chemical shifts and coupling constants as the proton thus confirming the stereochemistry of the product.

6. Electronic spectroscopy

The UV–Vis spectra of the 7-isocyanocoumarin complexes are shown in Fig. 5 and the UV–Vis and emission spectra of $PtMe_2(Idc)_2$ are shown in Fig. 6, respectively. The 7-isocyanocoumarin complexes have two prominent absorbance bands between 250 and 350 nm that are nearly identical in wavelength and general appearance

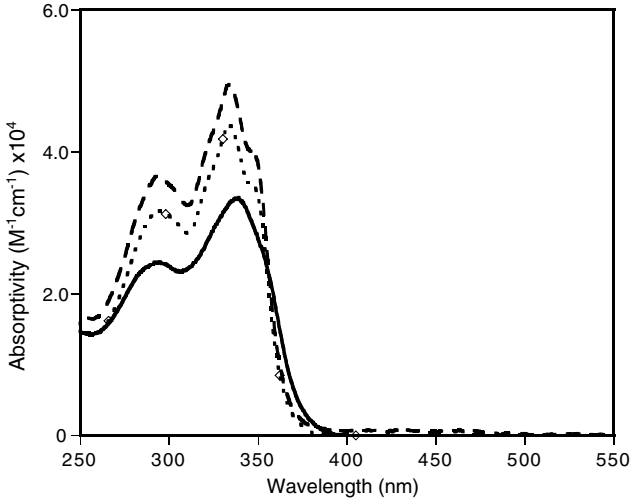


Fig. 5. Absorption spectra of PtL_2Me_2 complexes in methylene chloride solution (----- L = Mic; ·····L = Cmic; solid line L = Tic).

to both the spectra of the free ligands and to bands observed in the spectra of the $Mo(CO)_4$(7-isocyanocoumarin)$_2$ complexes [2]. This suggests that these bands can be assigned to ligand-centered transitions as they were in the Mo complexes. Surprisingly, there is no evidence for any Pt → coumarin charge transfer transitions. No room temperature emission was observed from these complexes. The absorption spectra of all three of the Idc complexes also display a striking resemblance to the absorbance spectrum of the free ligand, being dominated by an intense visible band with a high energy shoulder. One notable difference is that the band undergoes a ca. 20 nm red-shift in the complexes vs. the free ligand. We still assign these peaks to ligand-centered transition. The red-shift can be rationalized by considering the Pt as an electron-withdrawing substituent on the coumarin ring which stabilizes the ICT excited state by withdrawing a portion of the negative charge placed on the lactone carbonyl oxygen. The electron-withdrawing nature of the Pt is supported by the shift of the isocyanide CN stretching frequency to higher energy upon complexation.

Emission from both of the $PtR_2(Idc)_2$ complexes was observed at room temperature in dichloromethane solution upon excitation into the ligand-centered absorbance bands. The resulting emission spectrum for $Pt(Idc)_2Me_2$ is shown in Fig. 6. Emission data below 550 nm is omitted because of emission due to contamination by a small amount of the free Idc ligand. As with the absorbance bands, the emission profiles are similar in appearance to the emission from the free ligand, however the Stokes shift for the complexes is approximately double (135 vs. 70 nm) that observed for the free ligand. A similar effect was observed recently in platinum and iridium complexes of cyclometallated coumarin ligands [1a,24]. These complexes emit from ligand-centered

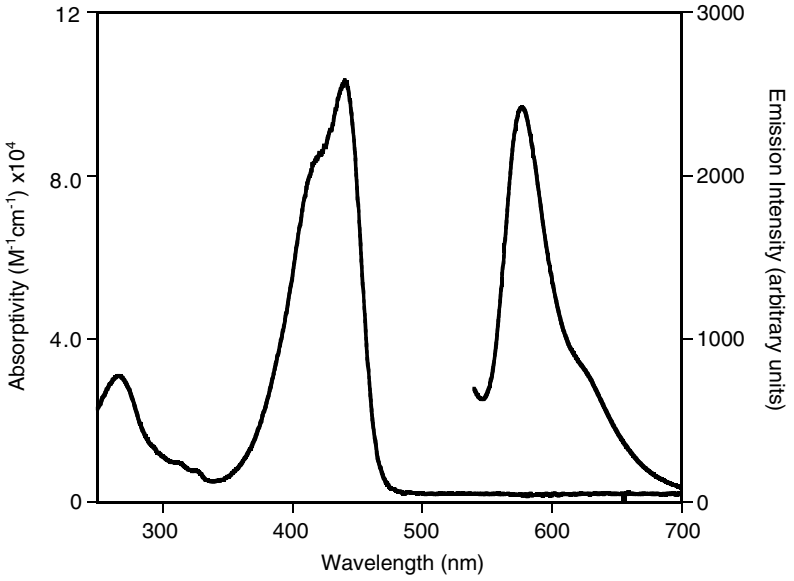


Fig. 6. Absorption and emission spectra of $Pt(Idc)_2Me_2$ in methylene chloride solution.

triplet states as opposed to the singlet emission observed from the free ligands. The rapid intersystem crossing in the ligand-centered excited state is attributed to the increased spin–orbit coupling induced by the presence of the heavy transition metals. The same explanation should be applicable to the $PtR_2(Idc)_2$ complexes, therefore, we assign the emission from these as arising from ligand-centered triplet states. The fact that we see no emission from the 7-isocyanocoumarin complexes strongly indicates that the emission cannot arise from charge transfer states. Surprisingly, no emission was observed from $PtMe_3(Idc)_2I$. The reason for this is not entirely clear, but it is possible that the ligand-centered excited state inter-system crosses to non-emissive metal-centered states. The lack of emission from many Pt(IV)–bipyridine complexes has been attributed to this cause [25] (see Table 2).

Table 2
UV–Vis absorption (λ_{max} in nm (ε in $cm^{-1}\,M^{-1} \times 10^4$)) and emission spectral data for Idc and Pt isocyanocoumarin compounds

	Absorption			Emission
	π–π*	π–π*	ICT	λ_{max}
Idc		262 (1.8)	420 (8.7)	490
$Pt(Idc)_2Me_2$		266 (2.9)	442 (10)	577
$Pt(Idc)_2Ph_2$		265 (3.0)	442 (9.6)	578
$Pt(Idc)_2Me_3I$		265 (3.8)	439 (8.7)	a
$Pt(Mic)_2Me_2$	293 (3.7)	334 (5.0)	a	a
$Pt(Tic)_2Me_2$	295 (2.4)	337 (3.3)	a	a
$Pt(Cmic)_2Me_2$	294 (3.2)	334 (4.4)	a	a

[a] Not observed.

7. Concluding remarks

A series of platinum (II) complexes, $PtR_2(CNR)_2$ R = methyl or phenyl, with isocyanocoumarin ligands have been synthesized and characterized. The absorption spectra of the 7-isocyanocoumarin complexes appear to display only ligand centered bands and unlike other square-planar Pt complexes, no evidence for MLCT or metal-centered bands arising from Pt–Pt interactions were observed. It is possible that the MLCT transitions are present, but are sufficiently high in energy to be masked by the intense ligand-centered bands. Intense visible absorption and emission bands were observed for the square planar Idc complexes assigned to ligand-centered excited states. It appears that changes in the Pt coordination sphere and oxidation state have little effect on the energy of the ligand-centered excited state since all of the Idc complexes have nearly identical absorption and emission maxima. It is intriguing that the ligand-centered emission was "switched off" by the oxidation of Pt(II) to Pt(IV). Future studies will focus on preparing Idc complexes in which the oxidation state of the metal can be easily and reversibly changed.

8. Experimental

8.1. General considerations

All reagents were purchased from Aldrich. Dichloromethane was distilled from P_2O_5 under nitrogen. All other reagents were used as received. Proton and carbon NMR spectra were recorded on a Varian or Joel 300 MHz spectrometer (proton 300 MHz, carbon 75.4 MHz) and referenced to $SiMe_4$. δ values are given in ppm and J values in Hz. Microanalyses were performed by MHW Laboratories, Phoenix, AZ. Infrared spectra

were recorded in methylene chloride solution using a Perkin–Elmer 1600 FT-IR spectrometer. Absorption spectra were recorded an Ocean Optics Chem 2000 fiber optic spectrometer. Emission spectra were recorded on an Ocean Optics S2000 CCD Array fiber optic spectrometer. Excitation at 405 nm was provided by a 200 W mercury vapor lamp using the appropriate interference filter. Emission from the sample was focused on to the fiber optic cable with a fiber-optic focusing assembly (Oriel). A 450 nm cut-off filter was placed over the focusing assembly to prevent interference from the excitation line. No corrections were made for grating efficiency and detector response.

9. X-ray diffraction analysis

A yellow rectangular plate ($0.04 \times 0.15 \times 0.35$ mm) was mounted on a glass fibre. Data were collected at −73 °C on a Nonius Kappa-CCD diffractometer using Nonius software [26]. Crystallographic measurements were done with graphite-monochromatized Mo Kα ($\lambda = 0.071073$) radiation using the ϕ/ω scan technique. 12,792 reflections were measured in the range $2.67 < \theta < 27.51°$, 6364 ($R_{int} = 0.057$) of which were independent reflections. Crystal cell refinement and data reduction (Lorentz and polarization effects as well as absorption) were carried out using DENZO-SMN [27]. The unit cell parameters [$a = 8.1790(2)$, $b = 8.4502(2)$, $c = 23.2226(9)$, $\alpha = 0.6780(10)°$, $\beta = 86.0480(10)°$, $\gamma = 62.6840(10)°$] were calculated and refined from the full data set.

The reflection data were consistent with a triclinic space group: $P\bar{1}$. The structure was solved by direct methods, using the SHELXS 97 computer program and refined using the SHELXL 97 computer program [28]. Two molecules [$C_{30}H_{34}N_4O_4Pt$] were found in the unit cell. The refinement of the structure was done on F^2 by the full-matrix least-squares method. All of the non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atom positions were calculated geometrically and were included as riding on their respective carbon atoms. The largest residue electron density peak (2.247 e/Å^3) was associated with the platinum atom. Full-matrix least-squares refinement on F^2 of 352 parameters converged to $R_1 = 5.07$ for 2σ data and $wR_2 = 12.04$ for all data.

10. Preparation of the compounds

Compounds [$Pt_2Me_4(\mu\text{-}SMe_2)_2$], **1**, and [$PtPh_2(SMe_2)_2$], **2**, were prepared as previously reported [29,30].

7-diethylamino-3-nitrocoumarin. Diethylaminosalicylaldehyde (5.0 g, 0.0259 mol), ethylnitroacetate (5.75 mL, 0.0259 mol), and toluene (75 mL) were added to a 100 mL flask equipped with a stir bar, reflux condensor, and Dean-Stark trap. Piperidine (0.25 mL) was then added. The solution was then refluxed for 24 h, cooled, and the resulting orange product was isolated by filtration. Recrystalization from 95% ethanol gave 5.46 g (80% yield) of orange needles. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.26$ [t, $^3J(H^{12}–H^{11}) = 7.1$, H^{12}]; 3.49 [q, $^3J(H^{11}–H^{12}) = 7.1$, H^{11}]; 6.48 [d, $^4J(H^8–H^6) = 2.5$, H^8]; 6.70 [dd, $^4J(H^6–H^8) = 2.5$, $^3J(H^6–H^5) = 9.1$, H^6]; 7.44 [d, $^3J(H^6–H^5) = 9.0$, H^5]; 8.72 [s, H^4].

7-diethylamino-3-formylcoumarin. 7-diethylamino-3-nitrocoumarin (2.0 g, 0.00763 mol), granular tin (4.0 g, 0.0343 mol), formic acid (20 mL), and toluene (40 mL) were added to a round bottom flask equipped with a stir bar, reflux condensor, and Dean-Stark trap. The mixture was refluxed for 14 h after which the heat was increased to distill off the formic acid. The solution was cooled and the supernatant was decanted off leaving a sticky orange solid. The solid was washed with ca. 150 mL of dichloromethane which was filtered through diatomaceous earth and concentrated by rotary evaporation. Addition of ether and cooling yielded 1.0 g of yellow crystals (51% yield). Anal. Calc. for $C_{14}H_{16}N_2O_3$: C, 64.60; H, 6.20; N, 10.76. Found: C, 64.65; H, 6.25; N, 10.83%.

7-diethylamino-3-isocyanocoumarin (Idc). A 50 mL flask was charges with 0.800 g (3.1 mmol) of 3-formyl-7-diethylaminecoumarin. Methylene chloride (15 mL) was added via syringe follwed by 3 mL of triethylamine added through a short column of activated alumina. Phosphorous oxychloride (0.29 mL, 3.1 mmol) was the added dropwise by syringe. The reaction was stirred for 30 min, during which time the formamide completely dissolved leaving a clear yellow solution. The reaction mixture was extracted with 2×10 mL portions of water and once with 10 mL of saturated NaCl solution. The methylene chloride layer was dried with anhydrous $MgSO_4$ and suction filtered through 5 cm of silica gel in a fritted funnel. The solvent was removed via rotary evaporation giving the product a yellow powder which was dried in vacuo (0.62 g, 83% yield). The crude product was suitable for synthesis. Chromatography on silica gel, eluting with methylene chloride, gave analytically pure material. Anal. Calc. for $C_{14}H_{14}N_2O_2$: C, 69.41; H, 5.82; N, 11.56. Found: C, 69.43; H, 5.79; N, 11.57%. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.29$ [t,$^3J(H^{12}–H^{11}) = 7$, H^{12}]; 3.35 [q, $^3J(H^{11}–H^{12}) = 7$, H^{11}]; 6.40 [d, $^4J(H^8–H^6) = 2$, H^8]; 6.55 [dd, $^4J(H^6–H^8) = 2$, $^3J(H^6–H^5) = 9$, H^6]; 7.19 [d, $^3J(H^5–H^6) = 9$, H^5]; 7.61 [s, H^4]. Selected IR: ν(CN) 2125(vs) cm^{-1}.

[$PtMe_2(Idc)_2$], **3**, was prepared by the reaction of 4 equivalents of isocyanocoumarin ligand with compound **1** (150 mg) in methylene chloride solution and allowed to stir for 2 h. The solvent was removed by evaporation and resulting solid washed twice diethyl ether (5 mL)

and under vacuum. Yield 80%. Crystals suitable for X-ray diffraction analysis were recrystallized from methylene chloride/methanol. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.77$ [s, ^2J(Pt–H) = 74, Me^a]; 1.26 [t, $^3J(H^{12}–H^{11}) = 7$, H^{12}]; 3.44 [q, $^3J(H^{11}–H^{12}) = 7$, H^{11}]; 6.48 [d, $^4J(H^8–H^6) = 2$, H^8]; 6.62 [dd, $^4J(H^6–H^8) = 2$, $^3J(H^6–H^5) = 9$, H^6]; 7.30 [d, $^3J(H^5–H^6) = 9$, H^5]; 7.81 [s, H^4]. Selected IR ν(CN) 2166(s), 2120(vs) cm^{-1}.

[PtMe$_2$(Mic)$_2$], **4**, was prepared similarly. Yield 80%. ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta = 0.697$ [s, ^2J(Pt–H) = 74, Me^a]; 2.43 [s, Me^4]; 6.34 [s, H^3]; 7.39 [d, $^3J(H^5–H^6) = 9$, H^5]; 7.66 [d, $^3J(H^6–H^5) = 9$, H^6]; 7.30 [apparent s, H^8]. Selected IR ν(CN) 2168(s), 2124(vs) cm^{-1}. Anal. Calc. for $C_{24}H_{20}N_2O_4Pt$: C, 48.4; H, 3.39; N, 4.71. Found: C, 48.3; H, 3.52; N, 4.73%.

[PtMe$_2$(Tic)$_2$], **5**, was prepared similarly. Yield 80%. ^{1}H NMR (300 MHz, $CDCl_3$): = 0.82 [s, ^2J(Pt–H) = 74, Me^a]; 6.90 [s, H^3]; 7.44 [dd, $^3J(H^5–H^6 = 8.5)$, $^4J(H^6–H^8) = 1.9$, H^6]; 7.78 [dq, $^3J(H^5–H^6) = 8.5$, $^5J(H^5–CF_3) = 1.6$, H^5]; 7.49 [d, $^4J(H^8–H^6) = 1.9$, H^8]. Selected IR ν(CN) 2168(s), 2115(vs) cm^{-1}. Anal. Calc. for $C_{24}H_{14}F_6N_2O_4Pt$: C, 41.0; H, 2.01; N, 3.98. Found: C, 41.2; H, 1.86; N, 3.98%.

[PtMe$_2$(Cmic)$_2$], **6**, was prepared similarly. Yield 80%. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.79$ [s, ^2J(Pt–H) = 74, Me^a]; 2.61 [s, Me^4]; 7.68 [m, H^5]; 7.41 [m, H^6]; 7.43 [m, H^8]. Selected IR ν(CN) 2169(s), 2123(vs) cm^{-1}. Anal. Calc. For $C_{24}H_{18}Cl_2N_2O_4Pt$: C, 43.8; H, 1.84; N, 4.26. Found: C, 44.0; H, 2.00; N, 4.19%.

[PtPh$_2$(Idc)$_2$], **7**, was prepared similarly except complex **2** was used as the platinum complex. Yield 70%. %. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 6.92$ [m, H^p, 1H]; 7.05 [m, H^m, 2H]; 7.44 [d, $^3J(H^o–H^m) = 7$, ^3J(Pt–H) = 64, H^o, 2H]; 1.22 [t, $^3J(H^{12}–H^{11}) = 6$, H^{12}]; 3.43 [q, $^3J(H^{11}–H^{12}) = 6$, H^{11}]; 6.45 [d, $^4J(H^8–H^6) = 2$, H^8, 1H]; 6.60 [dd, $^4J(H^6–H^8) = 2$, $^3J(H^6–H^5) = 7$, H^6, 1H]; 7.24 [d, $^3J(H^5–H^6) = 7$, H^5, 1H]; 7.70 [s, H^4, 1H]. Selected IR ν(CN) 2180(s), 2148(vs) cm^{-1}. Anal. Calc. for $C_{40}H_{38}N_4O_4Pt(0.25CH_2Cl_2)$: C, 56.6; H, 4.50; N, 6.56. Found: C, 56.6; H, 4.83; N, 6.20%.

[PtPh$_2$(Mic)$_2$], **8**, was prepared similarly. Yield 75%. $\delta = 6.45$ [m, H^p, 1H]; 7.75 [m, H^m, 2H]; 7.41 [dd, $^3J(H^o–H^m) = 8$, ^3J(Pt–H) = 63, $^4J(H^o–H^p) = 1$, H^o, 2H]; 2.45[m, Me^4]; 6.37 [m, H^3, 1H]; 7.63 [d, $^3J(H^5–H^6) = 8$, H^5, 1H]; 7.28 [dd, $^3J(H^6–H^5) = 8$, $^4J(H^6–H^8) = 2$, H^6, 1H]; 7.36 [d, $^4J(H^8–H^6) = 2$, H^8, 1H]. Selected IR ν(CN) 2183(s), 2146(vs) cm^{-1}. Anal. Calc. for $C_{34}H_{34}N_2O_4Pt$: C, 56.7; H, 3.34; N, 3.39. Found: C, 56.6; H, 3.72; N, 3.65%.

[PtMe$_3$I(Idc)$_2$], **9**, was prepared by oxidative addition of methyl iodide to complex **3**. Compound **7** (100 mg) was dissolved in acetone and a tenfold excess of methyl iodide was added in situ. The solution was stirred at room temperature for 24 h and the solvent removed by evaporation. The resulting solid was washed three times with diethyl ether (5 mL) and dried in vacuo. Yield 48 mg (59%). ^{1}H NMR (300 MHz, $CDCl_3$): = 1.36 [s, ^2J(Pt–H) = 63, Me^a]; 1.46 [s, ^2J(Pt–H) = 73, Me^b]; 1.24 [t, $^3J(H^{12}–H^{11}) = 7.5$, H^{12}]; 3.46 [q, $^3J(H^{11}–H^{12}) = 7.5$, H^{11}]; 6.44 [d, $^4J(H^8–H^6) = 2.2$, H^8]; 6.65 [dd, $^3J(H^6–H^5) = 9.3$, $^4J(H^6–H^8) = 2.2$, H^6]; 7.30 [d, $^3J(H^5–H^6) = 9.3$, H^5]; 7.90 [s, H^4]. ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = -2.86$ [J(Pt–C) = 513, Me^a]; 2.05 [J(Pt–C) = 577, Me^b]; 134.7 [J(Pt–C) = 701, C^{13}]; 45.5 [C^{11}]; 12.9 [C^{12}]; {97.4, 110.6, 130.5, 141.8 [$H^{4,5,6,8}$]}; 106.4,106.8,152.6,156.7 [$H^{2,3,7,9,10}$]. Selected IR ν(CN) 2194(s), 2181(vs) cm^{-1}. Anal. Calc. for C_{31} $H_{37}IN_4O_4Pt(0.5CH_2Cl_2)$: C, 42.3; H, 4.25; N, 6.26. Found: C, 42.1; H, 4.60; N, 5.83%.

[PtMe$_3$I(Tic)$_2$], **10**, was prepared similar to complex **9**. Yield 55%. ^{1}H NMR (300 MHz, $CDCl_3$): = 1.44 [s, ^2J(Pt–H) = 63, Me^a]; 1.45 [s, ^2J(Pt–H) = 71, Me^b]; 6.92 [q, $^4J(H^3–CF_3 = 1)$, H^3]; 7.85 [dq, $^3J(H^5–H^6) = 9$, $^5J(H^5–CF_3 = 1)$, H^5]; 7.55 [m, $H^{6,8}$]. Anal. Calc. for $C_{25}H_{17}F_6IN_2O_4Pt(0.5CH_2Cl_2)$: C, 34.5; H, 1.94; N, 3.16. Found: C, 34.5; H, 2.30; N, 2.90%.

11. Supplementary material

Crystallographic data for the structure analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 243903 for compound **3**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk.).

Acknowledgements

C.A. acknowledges the support of Orgometa. D.A.F. acknowledges the support of The Research Corporation who funded a portion of this work.

References

[1] (a) J. Brooks, Y. Babayan, S. Lamansky, P. Djurovich, I. Tsyba, R. Bau, M. Thompson, Inorg. Chem. 41 (2002) 3055;
(b) M. Hissler, J.E. McGarrah, W.B. Connick, D.K. Geiger, S.D. Cummings, R. Eisenberg, Coord. Chem. Rev. 208 (2000) 115;
(c) C.E. Whittle, J.A. Weinstein, M.W. George, K.S. Schanze, Inorg. Chem. 40 (2001) 4053;
(d) K.E. Dungey, B.D. Thompson, N.A.P. Kane-Maguire, L.L. Wright, Inorg. Chem. 39 (2000) 5192;
(e) M. Hissler, W.B. Connick, D.K. Geiger, J.E. McGarrah, D. Lipa, R.J. Lachicotte, R. Eisenberg, Inorg. Chem. 39 (2000) 447;
(f) W.B. Connick, D. Geiger, R. Eisenberg, Inorg. Chem. 38 (1999) 3264;
(g) W.B. Connick, V.M. Miskowski, V.H. Houlding, H.B. Gray, Inorg. Chem. 39 (2000) 2585;
(h) W. Paw, S.D. Cummings, M.A. Mansour, W.B. Connick, D.K. Geiger, R. Eisenberg, Coord. Chem. Rev. 171 (1998) 125;

(i) V.M. Miskowski, V.H. Houlding, Inorg. Chem. 30 (1991) 4446;
(j) V.M. Miskowski, V.H. Houlding, Inorg. Chem. 28 (1989) 1529;
(k) W. Lu, M.C.W. Chan, K.-K. Cheung, C.-M. Che, Organometallics 20 (2001) 2477;
(l) C.-W. Chan, L.-K. Cheng, C.-M. Che, Coord. Chem. Rev. 132 (1994) 87;
(m) N. Chaudhury, R.J. Puddephatt, J. Organomet. Chem. 84 (1975) 105;
(n) A. Von Zelewsky, P. Belser, P. Hayoz, R. Dux, X. Hua, A. Suckling, H. Stoeckli-Evans, Coord. Chem. Rev. 132 (1994) 75;
(o) A. Klein, J. van Slageren, S. Zaĺis, Inorg. Chem. 41 (2002) 5216;
(p) V. Balzani, A. Credi, M. Venturi, Coord. Chem. Rev. 171 (1998) 3;
(q) J.E. McGarrah, Y.-J. Kim, M. Hissler, R. Eisenberg, Inorg. Chem. 40 (2001) 4510;
(r) D.R. McMillin, J.J. Moore, Coord. Chem. Rev. 229 (2002) 113;
(s) J.F. Michalec, S.A. Bejune, D.G. Cuttell, G.C. Summerton, J.A. Gertenbach, J.S. Field, R.J. Haines, D.R. McMillin, Inorg. Chem. 40 (2001) 2193;
(t) J.H.K. Yip, Suwarno, J.J. Vittal, Inorg. Chem. 39 (2000) 3537;
(u) S. Lai, C. Chan, K. Cheung, C. Che, Organometallics 18 (1999) 3327;
(v) S.W. Lai, H.W. Lam, W. Lu, K.K. Cheung, C.M. Che, Organometallics 21 (2002) 226;
(w) T. Cheung, K. Cheung, S. Peng, C. Che, J. Chem. Soc., Dalton Trans. (1996) 1645;
(x) A. von Zelewsky, A.P. Suckling, H. Stoeckli-Evans, Inorg. Chem. 32 (1993) 4585;
(y) A. Klein, J. van Slageren, S. Zaĺis!, Eur. J. Inorg. Chem. (2003) 1927.

[2] D.A. Freedman, I. Keresztes, A.L. Asbury, J. Organomet. Chem. 642 (2002) 97–106.

[3] D.M. Manuta, A.J. Lees, Inorg. Chem. 25 (1986) 1354.

[4] A. Mayr, S. Wang, K.K. Cheung, M. Hong, J. Organomet. Chem. 684 (2003) 287.

[5] (a) M. Basato, F. Benetollo, G. Facchin, R.A. Michelin, M. Mozzon, S. Pugliese, P. Sgarbossa, S.M. Sbovata, A. Tassan, J. Organomet. Chem. 689 (2004) 454;
(b) Y.J. Kim, E.H. Choi, S.W. Lee, Organometallics 22 (2003) 3316.

[6] (a) M.S. Drew, D.E. Janzen, C.E. Buss, D.I. MacEwan, K.M. Dublin, K.R. Mann, J. Am. Chem. Soc. 123 (2001) 8414;
(b) S.M. Drew, D.E. Janzen, K.R. Mann, Anal. Chem. 74 (2002) 2547;
(c) C.E. Buss, K.R. Mann, J. Am. Chem. Soc. 124 (2002) 1031.

[7] K.T. Aye, R.J. Puddephatt, Inorg. Chim. Acta 235 (1995) 307.

[8] Robert Murray, Jesus Mendez, Stewart Brown, The Natural Coumarins: Occurance Chemistry, and Biochemistry, Wiley, New York, 1982.

[9] L.W. Wattenberg, L.K. Lam, A.V. Fladmoe, Cancer Res. 39 (1979) 1561;
R.G. Harvey, C. Cortez, T.P. Ananthanayaran, S. Schmolka, J. Org. Chem. 53 (1988) 3930.

[10] N.J. Turro, Modern Molecular Photochemistry, Benjamin/Cummings, Menlo Park, CA, 1978, p. 462;
G.G. Chimino, H.B. Gamper, S.T. Isaacs, J.E. Hearst, Ann. Rev. Biochem. 54 (1985) 1151.

[11] H.C. Clark, L.E. Manzer, J. Organomet. Chem. (1973) 411–428.

[12] S. Roy, R.J. Puddephatt, J.D. Scott, J. Chem. Soc., Dalton Trans. (1989) 2121.

[13] H.C. Clark, L.E. Manzer, Inorg. Chem. (1972) 2749.

[14] H.C. Clark, J.D. Ruddick, Inorg. Chem. (1970) 1226.

[15] F.H. Allen, A. Pidcock, J. Chem. Soc. (A) (1968) 2700.

[16] T.G. Appleton, H.C. Clark, L.E. Manzer, J. Organomet. Chem. (1974) 275–287.

[17] J.D. Ruddick, B.L. Shaw, J. Chem. Soc. (A) (1969) 2801.

[18] N.H. Dryden, R.J. Puddephatt, S. Roy, J.J. Vittal, Acta Crystallogr., Sect. C: Cryst. Struct. Commun. C50 (4) (1994) 533–536.

[19] (a) C. Anderson, M. Crespo, F. Rochon, J. Organomet. Chem. 631 (2001) 167;
(b) C. Anderson, M. Crespo, M. Font-Bardia, X. Solans, J. Organomet. Chem. 604/2 (2000) 178.

[20] L.M. Rendina, R.J. Puddephatt, Chem. Rev. 97 (1997) 1735.

[21] H.C. Clark, L.E. Manzer, J. Organomet. Chem. (1971) C89.

[22] G.A. Larkin, R. Mason, M.G.H. Wallbridge, J. Chem. Soc., Dalton Trans. (1975) 2305.

[23] (a) C.M. Anderson, R.J. Puddephatt, G. Ferguson, A.J. Lough, J.Chem. Soc., Chem. Commun. 18 (1989) 1297;
(b) C.M. Anderson, M. Crespo, M.C. Jennings, R.J. Puddephatt, G. Ferguson, A.J. Lough, Organometallics 10 (1991) 2672;
(c) M. Lashanizadehgan, M. Rashidi, J.E. Hux, S.S.M. Ling, R.J. Puddephatt, J. Organomet. Chem. 269 (1984) 317.

[24] (a) S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, H. Lee, C. Adachi, P.E. Burrows, S.R. Forrest, M.E. Thompsom, J. Am. Chem. Soc. 123 (2001) 4304;
(b) S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, R. Kwong, I. Tsyba, M. Bortz, B. Mui, R. Bau, M. Thompson, Inorg. Chem. 40 (2001) 1704.

[25] H. Kunkely, A. Vogler, Coord. Chem. Rev. 111 (1991) 15.

[26] Nonius KappaCCD Server Software. Windows 98 Version. Nonius BV, Delft, The Netherlands, 2003.

[27] Z. Otwinowski, W. Minor, in: C.W. CarterJr, R.M. Sweet (Eds.), DENZO-SMN, Methods in Enzymology, Macromolecular Crystallography, Part A, vol. 276, Academic Press, New York, 1997, pp. 307–326.

[28] G.M. Sheldrick, SHELXTL NT V6.12, University of Gottingen, Germany, 2002.

[29] G.S. Hill, M.J. Irwin, L.M. Rendina, R.J. Puddephatt, Inorg. Synth. 32 (1998) 149.

[30] M. Rashidi, Z. Fakhroeian, R.J. Puddephatt, J. Organomet. Chem. (1990) 261.