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Spectroelectrochemical studies on some new ruthenium(II) complexes containing both cyanide and isocyanide ligands

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Abstract

New ruthenium(II) complexes *trans*, *trans*, *trans*-$[RuCl_2(NCR)_2(CNR')_2]$ (R = Me or Ph, R′ = Bu^t, xylyl or cyclohexyl (cy)) have been prepared by treating *mer*-$[RuCl_3(NCR)_3]$ with the appropriate isocyanide ligand CNR′ in $EtOH/CH_2Cl_2$. These complexes have been shown to be oxidisable electrochemically in situ to the analogous ruthenium(III) species *trans*, *trans*, *trans*-$[RuCl_2(NCR)_2(CNR')_2]^+$ in 0.5 mol dm^{-3} $[NBu^n_4][PF_6]/CH_2Cl_2$ solution, the stereochemistry of the oxidised species being established by use of an infrared spectroelectrochemical (IRRAS) technique. The electronic absorption spectra of the ruthenium(III) species obtained by use of an OTTLE cell are also reported and discussed.

Keywords: Spectroelectrochemical studies; Ruthenium(II) complexes; Cyanide ligand; Isocyanide ligand

1. Introduction

There is much interest in redox-active ruthenium complexes which have been used, for example, as catalysts, as electrochromic materials and in energy storage devices. A wide range of such complexes can be formed with cyanide and isocyanide ligands [1]; thus the mixed chloride–cyanide complexes $[RuCl_{6-n}(NCR)_n]^z$ (R = Me or Ph, $n = 0$–6) have been prepared from $[RuCl_6]^{2-}$ by electrochemically induced displacement of chloride [2]. The ruthenium(III) isocyanide complexes *trans*-$[NBu^n_4][Ru(CNBu^t)_2X_4]$ (X = Cl or Br) undergo halide displacement upon reduction in acetonitrile [3,4], and their mixed-ligand environment also permits access to the ruthenium(IV) oxidation state. The ruthenium(II) isocyanide complexes *trans*-$[RuCl_2(CNR)_4]$ (R = Bu^t or xylyl) have been oxidised electrochemically to *trans*-$[RuCl_2(CNR)_4][ClO_4]$ in a $[NBu^n_4][ClO_4]$/MeCN solution [5]. Similar redox behaviour has also been reported for the complexes *trans*, *trans*, *trans*-$[RuCl_2(CNR)_2(PPh_3)_2]$ (R = Bu^t or xylyl) [5].

In this publication some new ruthenium(II) complexes, $[RuCl_2(NCR)_2(CNR')_2]$, containing both cyanide and isocyanide ligands, are described and their redox behaviour investigated by means of infrared reflection–absorption spectroscopy (IRRAS) [6] and by electronic spectroscopy with an optically transparent thin-layer electrochemical (OTTLE) [7] cell.

2. Experimental

Commercial $RuCl_3 \cdot xH_2O$ was obtained from Johnson Matthey. *tert*-Butylisocyanide and xylylisocyanide were purchased from Fluka and cyclohexylisocyanide was obtained from Aldrich. The complexes $[RuCl_3(NCPh)_3]$ and $[RuCl_3(NCMe)_3]$ were prepared by published methods [2] and their purity confirmed by elemental analysis (C, H, N). All the ruthenium(II) isocyanide complexes were prepared under a nitrogen atmosphere using standard Schlenk-line techniques.

2.1. $[RuCl_2(NCMe)_2(CNBu^t)_2]$ (**1**)

$[RuCl_3(NCMe)_3]$ (0.10 g, 0.30 mmol) and *tert*-butylisocyanide (0.14 g, 1.64 mmol) were dissolved in degassed 1:10 ethanol/dichloromethane (15 cm^3). The

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solution was heated under reflux for 2 h whereupon it changed from red to dark yellow. The insoluble by-products in the reaction flask were then filtered off under gravity and the filtrate volume was reduced to approximately 5 cm^3. A yellow product was precipitated on adding diethyl ether to the filtrate, separated off and recrystallised twice from CH_2Cl_2/diethyl ether solutions. Yield: 59%. *Anal.* Calc. for $C_{14}H_{24}N_4Cl_2Ru$: C, 40.0; H, 5.8; N, 13.3. Found: C, 39.8; H, 5.6; N, 12.7%.

The ^1H NMR spectrum of **1** recorded in $CDCl_3$ solution shows only the two signals ($\delta = 1.66$ and 2.42 ppm), as expected.

2.2. [RuCl$_2$(NCMe)$_2$(CNcy)$_2$] (2)

The complex was prepared in a similar manner to that used for $[RuCl_2(NCMe)_2(CNBu^t)_2]$ except that the reactants were heated under reflux for 4 h. The product is a yellow solid. Yield: 81%. *Anal.* Calc. for $C_{18}H_{28}N_4C_2Ru$: C, 45.7; H, 6.0; N, 11.8. Found: C, 45.2; H, 6.0; N, 11.4%.

2.3. [RuCl$_2$(NCMe)$_2$(CNxylyl)$_2$] (3)

$[RuCl_3(NCMe)_3]$ (0.10 g, 0.30 mmol) and xylylisocyanide (0.20 g, 1.52 mmol) were dissolved in degassed 1:10 ethanol/dichloromethane (15 cm^3) and approximately 0.2 g of mercury added. The mixture was heated under reflux for 1 h. The insoluble by-products and unreacted mercury in the reaction flask were filtered off under gravity and the filtrate volume reduced to approximately 5 cm^3. The yellow product which was precipitated on adding diethyl ether to the filtrate was recrystallised twice from CH_2Cl_2/diethyl ether solutions. Yield: 54% *Anal.* Calc. for $C_{22}H_{24}N_4Cl_2Ru$: C, 51.2; H, 4.7; N, 10.8. Found: C, 51.2; H, 4.4; N, 10.2%.

2.4. [RuCl$_2$(NCPh)$_2$(CNBu^t)$_2$] (4)

The complex was prepared in a similar manner to that used for $[RuCl_2(NCMe)_2(CNBu^t)_2]$. $[RuCl_3(NCPh)_3]$ was used instead of $[RuCl_3(NCMe)_3]$ and the reactants were heated under reflux for 3 h. The product is a yellow solid. Yield: 78%. *Anal.* Calc. for $C_{24}H_{28}N_4Cl_2Ru$: C, 52.9; H, 5.2; N, 10.3. Found: C, 52.5; H, 5.0; N, 10.3%.

2.5. [RuCl$_2$(NCPh)$_2$(CNcy)$_2$]·CH$_2$Cl$_2$ (5)

The complex was prepared in a similar manner to that used for $[RuCl_2(NCPh)_2(CNBu^t)_2]$ except that the reactants were heated under reflux for 4 h. The product is a yellow solid. Yield: 87%. *Anal.* Calc. for $C_{29}H_{34}N_4Cl_4Ru$: C, 51.1; H, 5.0; N, 8.2. Found: C, 51.7; H, 5.1; N, 8.3%.

2.6. [RuCl$_2$(NCPh)$_2$(CNxylyl)$_2$] (6)

The complex was prepared in a similar manner to that used for $[RuCl_2(NCMe)_2(CNxylyl)_2]$. $[RuCl_3(NCPh)_3]$ was used instead of $[RuCl_3(NCMe)_3]$. The product is a yellow solid. Yield: 78%. *Anal.* Calc. for $C_{32}H_{28}N_4Cl_2Ru$: C, 60.0; H, 4.4; N, 8.7. Found: C, 59.6; H, 4.3; N, 8.4%.

Cyclic voltammetric experiments involved the use of a PAR 174A polarographic analyzer and a PAR 175 waveform generator in conjunction with a Bryans Instruments 60000 Series X-Y/t chart recorder. The experiments were performed using a cell comprising a platinum working electrode, a platinum counter-electrode, and an Ag/AgCl reference electrode [8,9] calibrated against the ferrocenium–ferrocene couple (+0.55 V) [10]. The voltammetric data were not cor-

Table 1
Analytical data on the complexes

Complex number [a]	FAB mass spectral data [b,c] (*m*/*z*)	^{13}C NMR signal (ppm) [d]	
		NC	CN
1	420 (*M*); 379 (*M* − MeCN); 344 (*M* − Cl–MeCN); 337 (*M* − CNBu^t); 263 (*M* − Cl–MeCN–CNBu^t)	152	123
2	472 (*M*); 431 (*M* − MeCN); 396 (*M* − Cl–MeCN); 355 (*M* − Cl–2MeCN); 286 (*M* − Cl–CNcy–MeCN)	151	122
3	516 (*M*); 481 (*M* − Cl); 434 (*M* − 2MeCN); 362 (*M* − 2Cl–2MeCN); 307 (*M* − Cl–MeCN–CNxylyl)	164	122
4	544 (*M*); 509 (*M* − Cl); 461 (*M* − CNBu^t); 441 (*M* − PhCN); 406 (*M* − Cl–PhCN)	150	113
5	596 (*M* − CH$_2$Cl$_2$); 561 (*M* − Cl); 493 (*M* − PhCN); 458 (*M* − Cl–PhCN); 349 (*M* − Cl–PhCN–CNcy)	151	112
6	640 (*M*); 605 (*M* − Cl); 537 (*M* − PhCN); 502 (*M* − Cl–PhCN); 473 (*M* − Cl–CNxylyl)	163	112

[a] Refer to Section 2 for the identification of the complexes.

[b] Recorded in 3-nitrobenzyl alcohol matrix.

[c] *M* = molecular ion.

[d] Recorded in $CDCl_3$ solvent.

rected for the *IR* drop across the working and reference electrodes. The dichloromethane solvent was dried over KOH and distilled from CaH_2 prior to use; the supporting electrolyte, tetra-n-butylammonium hexafluorophosphate, was prepared as described previously [8,9]. Voltammetric and spectroelectrochemical experiments were carried out in 0.5 mol dm^{-3} $[NBu^n_4][PF_6]/CH_2Cl_2$.

Infrared (IR) spectroelectrochemical experiments were performed using an IRRAS cell mounted on a modified Specac specular reflectance attachment located in the sample compartment of a Nicolet Magna 750 FTIR spectrometer [6]. The electrode arrangement consisted of a highly polished platinum disc electrode (5 mm diameter), a platinum gauze counter-electrode, and a platinum wire pseudo-reference electrode. All spectroelectrochemical experiments were performed by first stepping to a potential of approximately 0.2 V past the appropriate $E_{1/2}$ and then collecting single-scan IR spectra (resolution = 1 cm^{-1}) as a function of time.

Ultraviolet–visible (UV–Vis) spectroelectrochemical experiments were performed using a cryostated OTTLE cell [7] positioned in the sample compartment of a Perkin–Elmer Lambda 16 spectrophotometer. The cell contained a platinum gauze working electrode (ca. 75% transmission), a platinum wire counter-electrode, and a platinum pseudo-reference electrode.

NMR spectra were recorded on a Bruker AMX 400 MHz spectrometer. Positive-ion FAB mass spectra were obtained with a VG ZAB 2SE mass spectrometer.

3. Results and discussion

The cyclohexylisocyanide and *tert*-butylisocyanide derivatives were prepared according to the following reaction scheme:

$$RuCl_3 \xrightarrow[\text{MeOH reflux}]{\text{NCR}} RuCl_3(NCR)_3 \xrightarrow[\text{EtOH/CH}_2\text{Cl}_2\text{ reflux}]{\text{CNR}'} RuCl_2(NCR)_2(CNR')_2$$

Reduction of $[RuCl_3(NCR)_3]$ under the stated conditions results in the elimination of a chloride and the facile replacement of one cyanide by isocyanide. $[RuCl_3(NCR)_3]$ complexes are thus found to be convenient precursors for the preparation of certain complexes of the type $[RuCl_2(NCR)_2(CNR')_2]$. It was found that mercury had to be used in the preparation of the xylylisocyanide derivatives because this ligand does not coordinate to ruthenium(III) under the specified conditions. However, the ruthenium(II) species produced by the mercury reduction readily coordinates to xylylisocyanide since the latter is a better π-acceptor than either cyclohexylisocyanide or *tert*-butylisocyanide [11]. All the products are stable in air and moderately soluble in dichloromethane. They were characterised by elemental

Table 2
Electrochemical and spectroelectrochemical data

Complex number [a]	$E_{1/2}$/V [b]	Electronic band maxima/cm^{-1} (ε/dm^3 mol^{-1} cm^{-1})		Band wavenumber/cm^{-1} [c,d]			
		Ru(II)	Ru(III)	Ru(II)		Ru(III)	
				ν_{NC}	ν_{CN}	ν_{NC}	ν_{CN}
1	+0.95	24 300 (1600) 38 200 sh (13 000)	19 000 sh, 20 300, 22 600, 31 700 sh, 41 700	2138	2287	2216	2333
2	+0.96	24 000 (1400) 38 200 (10 000) 42 700 (32 000)	19 000 sh, 20 300, 22 700, 37 000 sh, 41 500	2143	2288	2223	2334
3	+1.07	26 800 sh (960) 30 900 (16 000) 34 700 (30 000) 43 500 (36 000)	18 800 sh, 19 900, 22 500 sh, 37 000 sh, 41 500	2121	2291	2197	2334
4	+1.02	23 600 sh (1500) 26 500 (12 000) 33 000 (16 000) 43 700 (43 000)	19 400 sh, 20 900, 25 000 sh, 33 000 sh, 41 500	2142	2251	2216	2278
5	+1.02	23 900 (2500) 33 000 (10 000) 36 000 (10 000)	19 300 sh, 21 000, 23 600, 27 400 sh, 33 300, 36 200, 42 600	2150	2251	2223	2278
6	+1.15	24 000 sh (1000) 27 200 (13 000) 35 100 (41 000) 43 700 (54 000)	19 200 sh, 20 800, 25 600, 33 600, 39 000	2121	2254	2198	2276

[a] Refer to Section 2 for the identification of the complexes.

[b] Calibrated against ferrocenium–ferrocene couple (+0.55 V). The corresponding value for the *trans*, *trans*, *trans*-$[RuCl_2(CNBu^t)_2(MeCN)_2]^{0/+1}$ couple in MeCN is +0.94 V. The $E_{1/2}$ values are accurate to ±0.01 V.

[c] ν_{NC} refers to the wavenumber of the NC (isocyanide) stretch, ν_{CN} to that of the CN (cyanide) stretch.

[d] Recorded in CH_2Cl_2 solvent.

analysis, fast atom bombardment mass spectroscopy, ^{13}C NMR, IR and UV–Vis spectroscopy (Tables 1 and 2). The complexes gradually decompose over 24 h in air in dichloromethane solution. All attempts to grow single crystals of the complexes were unsuccessful.

Vibrational data for the complexes are reported in Table 2. Bands arising from cyanide (ν_{CN}) and isocyanide (ν_{NC}) stretching vibrations occur in the region 2100–2300 cm^{-1}. Each complex shows a single ν_{CN} and ν_{NC} band both in solution and in the solid state, implying that the complexes have a common structure in which each pair of the same ligands has the *trans* arrangement.

The electronic absorption spectra of the complexes (Table 2) each show a band in the 23 000–27 000 cm^{-1} region and two or more intense bands above 30 000 cm^{-1}. The less intense bands arise from MLCT transitions of the type $Ru(d\pi) \rightarrow CNR'(\pi^*)$, i.e. they involve excitation of metal $d\pi$ electrons into low-lying antibonding π orbitals of the isocyanide ligands. The charge transfer energies associated with these bands reflect the different π-acceptor capacities of the ligands, viz. $CNBu^t$, CNcy < CNxylyl. The more intense bands may arise from either MLCT or intraligand transitions.

The redox behaviour of the complexes was studied by cyclic voltammetry and the results are given in Table 2. The complexes exhibit quasi-reversible Ru(II)/Ru(III) oxidations in 0.5 mol dm^{-3} $[NBu^n_4][PF_6]/CH_2Cl_2$. Departure from reversible behaviour is indicated by ΔE_p values which increase with increasing scan rates and which are greater than the ideal Nernstian value of 59 mV (ΔE_p = separation between anodic and cathodic peak potentials). The $E_{1/2}$ values of the Ru(II)/Ru(III) oxidations also reflect the different π-acceptor capacities of the ligands, viz. NCMe < NCPh and $CNBu^t$, CNcy < CNxylyl.

Data relating to the IR spectroelectrochemical experiments on the complexes are reported in Table 2. The ν_{NC} and ν_{CN} bands in *trans*, *trans*, *trans*-$[RuCl_2(NCPh)_2(CNcy)_2]$ occur at 2150 and 2251 cm^{-1}, respectively (Fig. 1). Upon oxidation at + 1.2 V these bands collapse and new ones grow at 2223 and 2278 cm^{-1}, the former being assigned to ν_{NC} and the latter to ν_{CN}. The fact that only a single band occurs in each region implies that each product, like its precursor, has the *trans*, *trans*, *trans*-octahedral geometry. Each of the complexes could be reversibly oxidised in an IRRAS cell at room temperature, although the ratio, $I(\nu_{CN})/I(\nu_{NC})$, of the cyanide/isocyanide band intensities is less for the methylcyanide than for the phenylcyanide complexes (Fig. 2). The increase in both ν_{NC} and ν_{CN} on oxidation of Ru(II) to Ru(III) is consistent with generally accepted binding differences between these oxidation states.

Data relating to the UV–Vis spectroelectrochemical experiments are also reported in Table 2. The spectrum of *trans*, *trans*, *trans*-$[RuCl_2(NCPh)_2(CNcy)_2]$ shows bands arising from MLCT and intraligand transitions mainly in the UV region. Upon oxidation at + 1.2 V these bands collapse with the growth of bands at 22 600, 20 300 and 19 000 cm^{-1} (Fig. 3). The band at 19 000 cm^{-1} arises from a transition of the type $Cl(\pi) \rightarrow Ru(d\pi)$ while that at 20 300 cm^{-1} is due to a $CN(\pi) \rightarrow Ru(d\pi)$ transition [2,12]. The band observed at 22 600 cm^{-1} arises from a $NC(\pi) \rightarrow Ru(d\pi)$ transition, and in the spectrum of the analogous methylcyanide derivative, it is red-shifted as expected (Fig. 4). The other ruthenium complexes likewise each show intense bands in the 19 000–

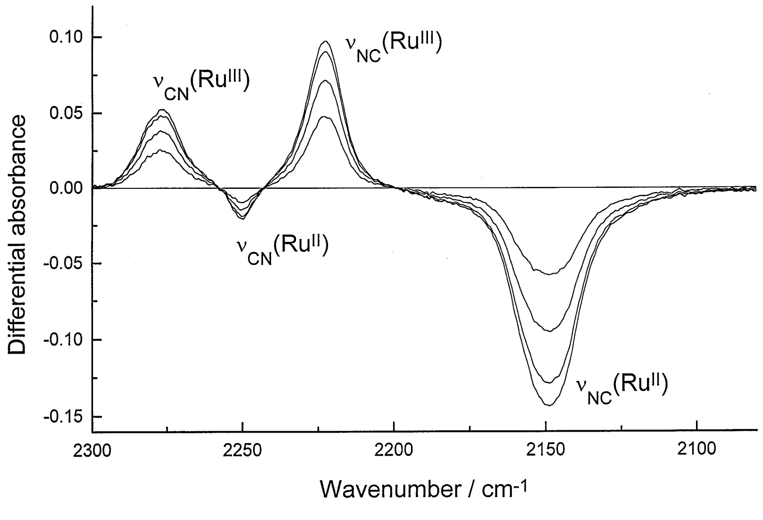

Fig. 1. Changes in the IR differential absorbance spectra upon oxidation of *trans*, *trans*, *trans*-$[RuCl_2(NCPh)_2(CNcy)_2]$ in an IRRAS cell at r.t.

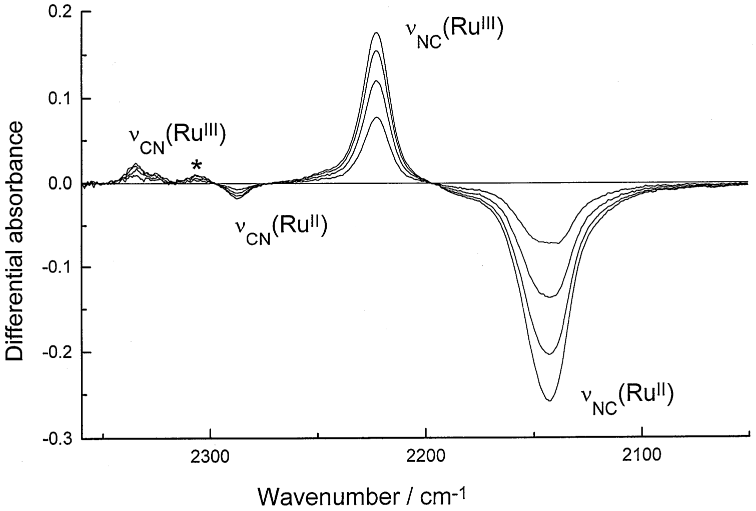

Fig. 2. Changes in the IR differential absorbance spectra of *trans*, *trans*, *trans*-[$RuCl_2(NCMe)_2(CNcy)_2$] upon oxidation in an IRRAS cell at r.t. A solvent peak (*) occurs at 2307 cm^{-1}.

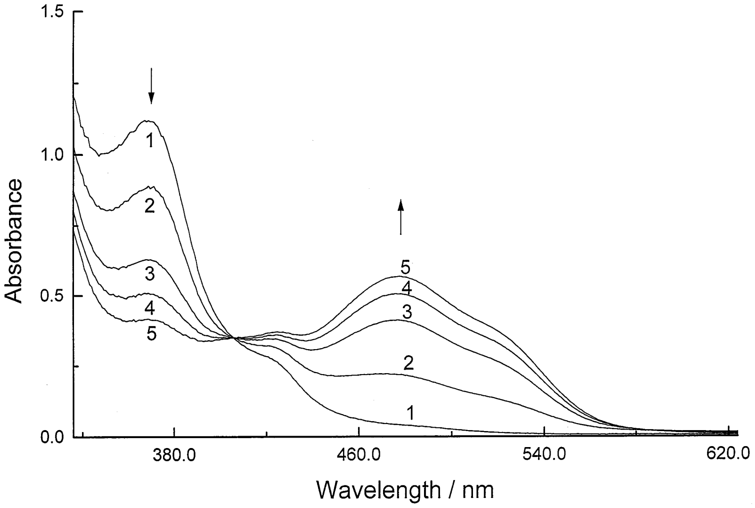

Fig. 3. Changes in the electronic spectrum of *trans*, *trans*, *trans*-[$RuCl_2(NCPh)_2(CNcy)_2$] upon oxidation in an OTTLE cell at r.t.

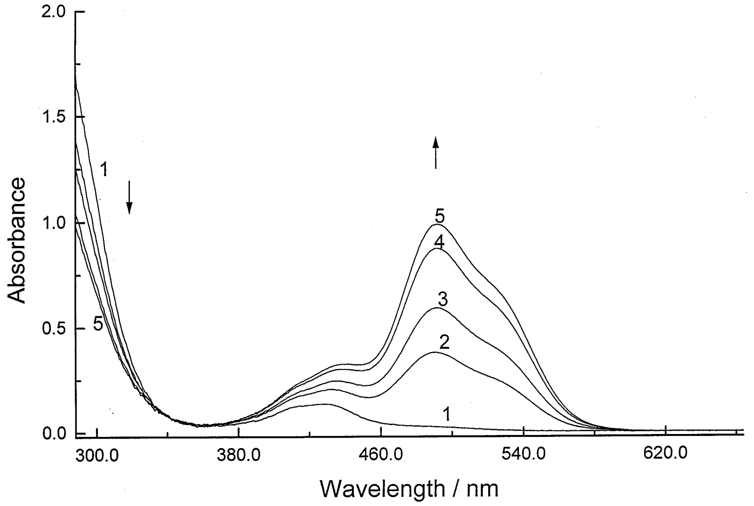

Fig. 4. Changes in the electronic spectrum of *trans*, *trans*, *trans*-[$RuCl_2(NCMe)_2(CNcy)_2$] upon oxidation in an OTTLE cell at r.t.

26 000 cm^{-1} region arising from similar LMCT transitions. Each of the ruthenium(II) complexes could be oxidised reversibly in an OTTLE cell at r.t. (Fig. 4).

4. Conclusion

The present research constitutes the first report of mixed cyanide/isocyanide complexes of ruthenium(II) and, by electrochemical generation, of their ruthenium(III) counterparts; all of the complexes possess the *trans*, *trans*, *trans*-octahedral geometry. The ruthenium(II) complexes are considered to be useful synthetically since their cyanide ligands are labile and can be replaced by π-acceptor ligands.

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