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fac-Re(CO)₃Cl Complexes of [2-(4-R-1*H*-1,2,3-Triazol-1yl)methyl]pyridine Inverse "Click" Ligands: A Systematic Synthetic, Spectroscopic, and Computational Study

Christopher B. Anderson,[†] Anastasia B. S. Elliott,^{†,‡} C. John McAdam,[†] Keith C. Gordon,^{†,‡} and James D. Crowley^{*,†}

[†]Department of Chemistry and [‡]MacDiarmid Institute for Advanced Materials and Nanotechnology, University of Otago, P.O. Box 56, Dunedin, New Zealand

Supporting Information

ABSTRACT: A series of electronically tuned fac-Re(CO)₃Cl inverse pyridyl-1,2,3-triazole complexes have been synthesized in good to excellent yields (72–95%) by refluxing methanol solutions of [Re(CO)₅Cl] and the substituted [2-(4-R-1*H*-1,2,3-triazol-1-yl)methyl]pyridine ligands (py(CH₂)tri-R). The resulting rhenium(I) complexes were characterized by elemental analysis, HR-ESI-MS and IR and ¹H and ¹³C NMR spectroscopy. Additionally, the molecular structures of three of the complexes were confirmed using X-ray crystallography. The electronic properties of this series of *fac*-[(py(CH₂)tri-R)Re(CO)₃Cl] complexes were examined using UV– vis, Raman, and emission spectroscopy and cyclic voltammetry techniques. The complexes exhibit intense absorptions in the UV



region, which were modeled using time-dependent density functional theory (TD-DFT). The calculations suggest that the lower energy part of the absorption band is MLCT in nature and additional higher energy $\pi - \pi^*$ transitions are present. The electronic spectra are nearly identical for all except where R = 4-nitrophenyl, suggesting that the 1,2,3-triazolyl unit acts as an electronic insulator. The TD-DFT calculations suggest that the lowest energy MLCT transition is polarized to the pyridine moiety for all complexes except the nitro-substituted one. With R = 4-nitrophenyl the MLCT is directed to an acceptor MO polarized to the triazole-R moiety. This finding is supported by resonance Raman studies that show enhancement of modes associated with the triazole-R group. The complexes are weakly emissive at room temperature with quantum yields <10⁻³ and correspondingly short excited-state lifetimes ($\tau < 20$ ns). The electrochemistry of the complexes is defined by quasi-reversible Re oxidation and irreversible triazole-based ligand reduction processes. The nitro-substituted complexes show additional nitrobenzene-type reduction features. Consistent with the spectroscopic data, the positions of the oxidation and reduction processes are essentially unaffected by the electronic nature of the 2-(4-R-1H-1,2,3-triazol-1-yl)pyridine substituent.

INTRODUCTION

There has been almost 40 years¹ of intense interest in complexes with the general formula fac-[Re(N^N)(L)(CO)₃] (where N^N is a neutral conjugated diimine ligand such as 2,2'-bipyridine (bipy, 1; Figure 1) or 1,10-phenanthroline (phen, 1) and L is an ancillary ligand) due to their rich photophysical



Figure 1. Bidentate N^N chelators 2,2'-bipyridine (bipy, 1), 1,10-phenanthroline (phen, 1), 2-(1-R-1H-1,2,3-triazol-4-yl)pyridines (2), and [(4-R-1H-1,2,3-triazol-1-yl)methyl]pyridines (3).

properties.^{2,3} Complexes of this type have been exploited as components of luminescent⁴ and light-harvesting materials⁵ and as photocatalysts for the reduction of CO_2 .^{6,7} A range of luminescent sensors and metallosupramolecular architectures have also been developed from the diimine rhenium(I) tricarbonyl motif.⁸ Additionally, bioconjugated [Re(N^N)(L)-(CO)₃] complexes have been examined as diagnostic imaging and therapeutic agents.⁹ All these applications have made use of substituted bipy or phen chelating units, but more recently, as part of efforts to generate new photophysical properties, rhenium(I) tricarbonyl complexes with other N[^]N¹⁰ and N[^]C¹¹ bidentate chelate ligands have been explored.

The 2-(1-R-1*H*-1,2,3-triazol-4-yl)pyridine (pytri-R, **2**) and [(4-R-1H-1,2,3-triazol-1-yl)methyl]pyridine (py(CH₂)tri-R,**3**) "click" ligands have emerged as readily modified bipy and phen

Received: September 12, 2012 Published: January 30, 2013 surrogates.¹² These compounds are synthesized using the functional group tolerant Cu(I)-catalyzed 1,3-cycloaddition of organic azides with terminal alkynes (the CuAAC reaction),¹³ which enables the rapid generation of a wide range of functionalized ligands. This has meant that complexes of these ligands have been applied to the development of electronic^{14,15} and luminescent^{16,17} materials, catalysts,¹⁸ and metallo-pharmaceuticals.¹⁹

Several different research groups have synthesized [Re(pytri- $R(CO)_3Cl$ complexes and examined their use for the development of luminescent bioprobes.^{20,21} Building on that work, we recently synthesized a family of electronically tuned [Re(pytri-R)(CO)₃Cl] complexes in an attempt to systematically modulate the photophysical properties of the fac-Re(CO)₃Cl motif.²² Interestingly, the MLCT transition energy and the emission maxima were unaffected by the nature of the R substituent on the 2-(1-R-1H-1,2,3-triazol-4-yl)pyridine ligand, indicating that the 1,2,3-triazolyl unit was acting as an electronic insulator. Here we have synthesized and characterized an analogous series of electronically modified fac-Re(CO)₃Cl complexes of the "inverse" pyridyl-1,2,3-triazole ligand 3 in order to examine whether the observed insulator effect is dependent on the substitution pattern of the 1,2,3triazole unit. DFT calculations, UV-vis, Raman, and emission spectroscopy, and cyclic voltammetry techniques were used to examine the electronic structures of this series of complexes and compare them to those of the analogous family incorporating the regular "click" ligand 2.

RESULTS AND DISCUSSION

Ligand Synthesis and Characterization. The ligands 3a-f were synthesized in good to excellent yields (68–91%) using the standard Fokin²³ conditions (Scheme 1(i)) that we have exploited previously for the synthesis of these and related compounds.^{24–26} The new ligand 3e was characterized by elemental analysis, HR-ESI-MS, IR, ¹H and ¹³C NMR spectroscopy, whereas the identity of the known ligands 3a-d,f was confirmed by ¹H NMR spectroscopy and HR-ESI-MS (Supporting Information).²⁷

Synthesis of Re(I) Complexes. The rhenium(I) complexes were prepared using the method previously exploited to synthesize the related 2-(1-R-1*H*-1,2,3-triazol-4-yl)pyridine *fac*-[Re(CO)₃Cl] complexes.^{21,22} One of the ligands (**3a**–**f**, 1 equiv) was added to a methanol solution of [Re(CO)₅Cl] (1 equiv), and the resulting reaction mixture was heated at reflux for 16 h (Scheme 1(ii)). The reaction mixtures were then cooled to room temperature. In some cases this resulted in the precipitation of the rhenium(I) complexes from solution. In other cases the addition of diethyl ether or petroleum ether to the reaction mixtures led to the precipitation of white-pale yellow microcrystalline powders which were isolated by filtration in excellent yields (72–95%). The complexes have been characterized using elemental analysis, HR-ESI-MS, IR, ¹H and ¹³C NMR spectroscopy (Supporting Information).

IR spectra of the isolated colorless solids show absorption bands resulting from C–H stretching (3100–2900 cm⁻¹) and from the skeletal vibrations of the aromatic rings (1600–1400 cm⁻¹), confirming the presence of the ligands in the isolated materials. Additionally, three strong ν (CO) stretching bands are observed in the region 2029–1882 cm⁻¹, indicative of the presence of the *fac*-[Re(CO)₃Cl] core (Supporting Information). Unequivocal proof of this facial (*fac*) coordination geometry was obtained from X-ray crystallography (vide infra). Scheme 1. ^a



^{*a*}Legend: (i) NaN₃, CuSO₄·5H₂O or Cu(OAc)₂, ascorbic acid, Na₂CO₃, DMF/H₂O (4:1), room temperature, 20 h; (ii) [Re-(CO)₅Cl], MeOH, 70 °C, 16 h.

The values of the ν (CO) stretching bands are very similar to those observed for related *fac*-[(1 or 2)Re(CO)₃Cl] complexes (range 2029–1881 cm⁻¹), suggesting that the strength of the rhenium–ligand interaction in these complexes is comparable.^{22,28} This is somewhat surprising, as it has been shown that 1 and 2 form more stable complexes than 3 with other metal ions.^{24,29}

Elemental analysis indicated that these bidentate "click" ligands 3a-f formed rhenium(I) complexes with a 1:1 metal:ligand ratio. Consistently, the HR-ESI-MS spectra (acetonitrile) of the complexes showed major ions due to $[(L)Re(CO)_3Cl](Na)^+$ and $[(L)Re(CO)_3]^+$, which displayed the expected Re^{185/187} isotope patterns (Supporting Information).

¹H NMR spectra of the rhenium(I) complexes 4a-e were recorded at room temperature in d_6 -acetone (Figure 2 and Supporting Information), and in general, the spectra show a simple pattern containing one set of proton signals, suggesting the quantitative formation of single metal containing species. In

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Figure 2. Partial ¹H NMR spectra (400 MHz, d_6 -acetone, 298 K, 2 mM) of the ligand 3a and the rhenium(I) complexes 4a–f.

comparison with the spectra of the ligands 3a-f, the proton signals of the corresponding rhenium(I) complexes are sharp and shifted downfield, indicative of metal complexation in solution. The large downfield shift of the pyridyl (H_a) and triazole (H_{e}) proton signals indicates that the ligands are acting, as expected, as bidentate chelates. Additionally, the two methylene (H_d) protons of the [2-(4-R-1H-1,2,3-triazol-1yl)methyl]pyridine ligands, which are observed as a singlet in the proton NMR of the free ligands, are split into two doublets in the complexes. The observed AB coupling pattern (I = 15 -16 Hz) is due to geminal interactions between two inequivalent protons and is also indicative of a bidentate coordination mode. The complexes 4a-f are chiral and exist in solution as racemic mixtures, except in the case of the steroid complex 4f. Because the steroid substituent is also chiral, a ~1:1 mixture of diastereisomers is formed in this case, as shown by the ¹H NMR spectrum of 4f (Figure 2). Attempts to separate these two isomers by chromatography were unsuccessful.

The molecular structures of the rhenium(I) complexes 4a.d. and e (Figure 3, Table 1, and Supporting Information Table S1) were unambiguously confirmed by X-ray crystallography. X-ray-quality single crystals were obtained by vapor diffusion of either methanol or diethyl ether into dilute acetone solutions of the metal complexes. The Re(I) complexes formed with the [(4-R-1*H*-1,2,3-triazol-1-yl)methyl]pyridine series of ligands all crystallized in the triclinic space group $P\overline{1}$. As expected, the inverse click ligands are coordinated to the rhenium(I) center in a bidentate fashion through the pyridyl and triazole nitrogen atoms. A chloride and three carbonyl ligands are also bound to the rhenium in the expected facial array, leading to a distortedoctahedral coordination environment at the metal center. The presence of a methylene spacer between the triazole and pyridyl groups leads to the formation of a six-membered chelate ring, and the bite angles of the ligands vary little, ranging from 81.98(8) to 83.5(3)°. The six-membered rings formed by chelation of the ligand to the metal center adopt boat conformations with the fold angles between the pyridyl and triazole rings ranging from 111.09 to 114.22°. Altering the substituent on the triazole ring has little effect on the metric parameters of the rhenium complexes, suggesting that there is very little electronic tuning of the ligand characteristics upon side-arm substitution. In addition, the N_{py}-Re bonds (2.198(5)-2.218(9) Å) are consistently longer than the N_{trz}-Re bonds (2.155(2)-2.180(7) Å); this behavior has



Figure 3. Molecular structures of (a) **4a**, (b) **4d**, and (c) **4e** shown as ORTEP diagrams. The thermal ellipsoids are shown at the 50% probability level. Solvent molecules are omitted for clarity. The phenyl substituent of **4a** is disordered over two sites; only one orientation is shown.

been observed in other metal complexes of these [(4-R-1*H*-1,2,3-triazol-1-yl)methyl]pyridine ligands. A number of experimental^{14,24,30} and theoretical studies have shown that the related "regular" 2-(1-R-1*H*-1,2,3-triazol-4-yl)pyridine ligands form more stable complexes than the [(4-R-1*H*-1,2,3-triazol-1-yl)methyl]pyridine inverse "click" chelators. Interestingly, the Re–N3_{trz} and Re–N2_{trz} bond lengths are remarkably similar throughout the entire series of regular five-membered^{21,22} and inverse six-membered [(N^N)Re(CO)₃Cl] "click" complexes that have been studied (Supporting Information Table S2), regardless of whether the triazole is coordinated to the Re center through N2 or N3. Similar behavior has been observed for Pd(II) complexes of these ligands.²⁴

In the extended crystal structures the complexes 4a and d form double-stranded supramolecular polymers that are held together by C–H- - -Cl hydrogen bonds^{30,31} and either CH- π or face-to-face π -stacking interactions (Figure 4 and Supporting Information). In 4a the chloride of one complex hydrogen bonds to the acidic methylene CH (Cl- - -H = 2.638(2) Å,

	4a	4d	4e
	Bond Leng	ths (Å)	
$\operatorname{Re}(1) - \operatorname{N}(1)$	2.198(5), 2.291	2.218(9), 2.272	2.214(2), 2.271
Re(1)–N(3)	2.164(5), 2.215	2.180(7), 2.205	2.155(2), 2.20 7
Re(1)-C(21)	1.896(8), 1.926	1.940(11), 1.931	1.921(3), 1.930
Re(1)-C(22)	1.921(8), 1.922	1.945(10), 1.925	1.921(3), 1.926
Re(1)-C(23)	1.907(8), 1.915	1.922(11), 1.914	1.925(3), 1.914
Re(1)-Cl(1)	2.4741(18), 2.540	2.481(3), 2.513	2.4791(7), 2.513
	Bond Angle	s (deg)	
N(1)-Re(1)-N(3)	82.88(19), 82.6	83.5(3), 82.6	81.98(8), 82.3
N(1)-Re(1)-C(21)	172.7(3), 175.0	174.2(4), 171.8	172.12(10), 171.8
N(1)-Re(1)-C(22)	94.5(3), 94.1	95.0(4), 94.1	95.97(10), 94.2
N(1)-Re(1)-C(23)	97.0(3), 90.9	95.5(4), 94.9	93.81(10), 94.9
N(1)-Re(1)-Cl(1)	83.16(13), 86.9	83.5(2), 81. 7	84.50(6), 82.0
N(3)-Re(1)-C(21)	92.7(3), 92.8	92.8(4), 92.3	93.32(10), 92.5
N(3)-Re(1)-C(22)	175.2(2), 176.0	178.3(4), 174.9	177.11(10), 174.8
N(3)-Re(1)-C(23)	95.4(3), 90.4	92.9(4), 93.1	94.37(11), 93.2
N(3)-Re(1)-Cl(1)	85.36(14), 87.7	83.8(2), 85.2	83.68(6), 85.3
C(21)-Re(1)-Cl(1)	90.7(3), 90. 7	91.7(3), 91.5	88.71(9), 91.3
C(21)-Re(1)-C(22)	89.5(3), 90.1	88.8(4), 90.4	88.49(12), 90.4
C(21)-Re(1)-C(23)	89.2(4), 91.2	89.1(4), 91.6	92.85(12), 91.6
C(22)-Re(1)-Cl(1)	90.4(2), 89.7	96.7(3), 90.4	94.12(9), 90.3
C(22)-Re(1)-C(23)	88.8(3), 92.0	86.5(4), 90.9	87.78(12), 90.9
C(23)-Re(1)-Cl(1)	179.3(2), 177.3	176.7(3), 176.5	177.58(9), 176.8
^a Calculated values (DFT, B3LYP) are s	hown in boldface.		

Table 1. Selected Bond Lengths (Å) and Angles (deg) of the Rhenium(I) Inverse "Click" Complexes^a

Cl- - -C = 3.569(7) Å) on an adjacent complex, leading to the formation of a single-stranded linear polymer. Two of these strands interact through a face-to-face π -stacking interaction (centroid-centroid distance 3.736 Å) between the phenyl group and the 1,2,3-triazole units on adjacent complexes to generate the double-stranded structure (Figure 4a and Supporting Information). A similar hydrogen-bonding interaction (Cl- - -H = 2.593(2) Å, Cl- - -C = 3.53(7) Å) is found in 4d; these linear strands interact with a neighboring polymer through CH- π interactions between the benzyl substituent methylene hydrogens and the phenyl unit of the adjacent complex (CH-centroid distances 3.032 and 3.122 Å) (Figure 4b and Supporting Information). The caffeine-substituted complex 4e adopts a different supramolecular structure; the individual complexes fold into a U-shaped conformation and two complexes interact through C-H---O hydrogen bonds $(O_{-} - H = 2.358(2), O_{-} - C = 3.124(7) \text{ Å})$ between a carbonyl of the caffeine substituent and an acidic CH on the pyridyl ring. This interaction generates a supramolecular cage that is filled with two acetone solvent molecules. The cages form a slipped stacked polymer through face-to-face π -stacking interactions (centroid-centroid distance 3.381 Å) between the caffeine groups (Figure 4c and Supporting Information).

Photophysical Properties and DFT Calculations. A number of spectroscopic and computational methods were used to investigate the electronic structure of 4a-f. Density functional theory (DFT) and time-dependent (TD) DFT calculations were performed using the B3LYP and CAM-B3LYP functionals (respectively) and 6-31G(d) and LANL2DZ basis sets for small atoms and Re, respectively. These calculations were checked for accuracy by comparison to X-ray crystallographic data obtained for 4a,d and e (Table 1). The experimental values of a number of coordinating bonds and angles are tabulated and show good agreement with those

obtained from calculations, with bond lengths differing by less than 0.1 Å and angles by 7° or less. 32

In addition to comparing experimental and calculated structures, vibrational spectra were also examined. In an effort to quantify how well the experimental and simulated spectra match, the mean absolute deviations (MAD) of analogous bands between 400 and 1650 cm⁻¹ were calculated. A MAD of 10 cm⁻¹ or less is considered to indicate that the computational modeling is accurate enough to use for prediction of less easily measured, electronic properties.^{32–34} Figure 5 shows a typical comparison for 4b in which a MAD of 7 cm⁻¹ was found. The other complexes were calculated as having MADs of 10, 9, 9, 10, and 10 for 4a,c-f, respectively.

The electronic absorption spectra of 4a-f are shown in Figure 6. These show a strong band at \sim 250 nm and a weaker one at \sim 290 nm, except in the case of 4b. The 4-nitrophenylsubstituted complex 4b also shows these transitions; however, the 250 nm band is shifted to ~275 nm (along with 4e) in addition to displaying a different intensity profile. The calculated TD-DFT results are summarized and compared to experiment in Table 2, including a comparison of electron transition density changes. TD-DFT predicts that the lower energy band of all complexes (except 4b), at around 290 nm and predicted at ~330 nm, is MLCT in nature with most of the electron density based on the pyridine section of the ligand (Figure 7). In fact, all predicted transitions for 4d and f are MLCT in nature. The remaining complexes' higher energy transition, observed at around 255 nm and calculated at 240 nm, is predicted to be more $\pi - \pi^*$ in nature and centered on the R substituent. However, a reasonable amount of MLCT character is still observed. These assignments for the two major transitions are in agreement with those found for a similar series of complexes based on the ligand 2.22 Similarly to the previous study, neither the experimental nor the calculated transitions show significant shifts with differing substituents,

a)

b)

c)



Figure 4. Mercury diagrams showing the extended packing present in the solid-state structures of (a) 4a, (b) 4d, and (c) 4e. Color scheme: gray, carbon; blue, nitrogen; teal, rhenium; red, oxygen; white, hydrogen.

except in the case of **4b**. Compound **4f** displays an extra shoulder transition at 287 nm, which TD-DFT predicts to be of MLCT character.

The 4-nitrophenyl-substituted complex 4b is the only material reported here with a significantly different electronic absorption spectrum. TD-DFT is consistent with this finding and predicts that the lower energy band at 302 nm (predicted at 282 nm) involves a donor molecular orbital (MO) spread over the metal center and an acceptor MO based on the 4-nitrophenyl (Figure 8). The higher energy transition at 271 nm, predicted at 288 nm, is similar in nature but with an additional small contribution from the R substituent to the donor orbital. This is not inconsistent with the other complexes, just with a smaller -R contribution.



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Figure 5. Comparison of simulated (upper, blue trace) Raman spectrum of 4b with the experimental FT-Raman spectrum (lower, black trace).



Figure 6. Electronic absorption spectra of 4a-f obtained at 10^{-5} M concentrations in CH₃CN.

The nature of electronic transitions can also be probed by the use of resonance Raman spectroscopy. This technique involves exciting the sample with a laser wavelength that is coincident with the electronic transition. Raman band intensities are enhanced by up to 10^6 depending on the nature of the vibration; that is, modes that mimic the electronic transition undergo enhancement.^{3,33,35} Using the pattern of Raman band enhancements in concert with knowledge of the nature of the vibrational modes, gained from DFT frequency calculations, we can probe the electronic transitions. Resonance Raman spectra using 350.7 nm excitation showed limited enhancement of a few modes for 4b and c; no usable spectra could be obtained for the other complexes (Figure 9). It is possible to use the enhancement patterns to ascertain if the MLCT transition is polarized on either the pyridine or triazole moiety. This can be

Tab	le 2.	Co	mparison	of	Experimenta	ΙE	lectronic	Absor	ption	Data	with	TD	-DFT	Calcu	lations	for	4a-	-f
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	exptl				calcd ^a	electron transition density change b (%)					
compd	λ/nm	ε/L M ⁻¹ cm ⁻¹	$\lambda/$ nm	F	confign (coeff)	Re(CO) ₃ Cl	pyridine	triazole– CH ₂	-R		
4a	251	24100	236	0.235	H-4 \rightarrow L+3 (0.17), H-3 \rightarrow L+3 (0.18), H \rightarrow L+3 (0.14)	$\begin{array}{c} 42 \rightarrow 7 \\ (-35) \end{array}$	$\begin{array}{c} 1 \rightarrow 23 \\ (22) \end{array}$	$\begin{array}{c} 12 \rightarrow 22 \\ (10) \end{array}$	$\begin{array}{c} 46 \rightarrow 48 \\ (2) \end{array}$		
	286 (sh)	10000	332	0.0391	H-1 \rightarrow L (0.82), H \rightarrow L (0.10)	$\begin{array}{c} 96 \rightarrow 5 \\ (-91) \end{array}$	$\begin{array}{c} 2 \rightarrow 88 \\ (86) \end{array}$	$2 \rightarrow 7 (5)$	$1 \rightarrow 0 \; (-1)$		
4b	271 (sh)	21500	259	0.2849	$\begin{array}{l} \text{H-6} \rightarrow \text{L} \mbox{ (0.15), H-5} \rightarrow \text{L} \mbox{ (0.14), H-3} \rightarrow \text{L} \mbox{ (0.36),} \\ \text{H-1} \rightarrow \text{L} \mbox{ (0.11)} \end{array}$	$\begin{array}{c} 49 \rightarrow 1 \\ (-48) \end{array}$	$1 \rightarrow 2 (1)$	$\begin{array}{c} 14 \rightarrow 11 \\ (-3) \end{array}$	$\begin{array}{c} 36 \rightarrow 87 \\ (51) \end{array}$		
	302	22800	282	0.2203	H-3 → L (0.10), H-1 → L (0.50), H-1 → L+6 (0.14), H → L (0.10)	$\begin{array}{c} 87 \rightarrow 14 \\ (-73) \end{array}$	$1 \rightarrow 2 (1)$	$7 \rightarrow 10 (3)$	$5 \rightarrow 74 \\ (69)$		
4c	258	34400	242	0.4691	H-2 \rightarrow L+3 (0.31), H \rightarrow L+3 (0.24)	$\begin{array}{c} 48 \rightarrow 5 \\ (-43) \end{array}$	$\begin{array}{c} 0 \rightarrow 16 \\ (16) \end{array}$	$\begin{array}{c} 11 \rightarrow 33 \\ (22) \end{array}$	$\begin{array}{c} 41 \rightarrow 46 \\ (5) \end{array}$		
	301 (sh)	11500	332	0.0403	H-1 \rightarrow L (0.66), H \rightarrow L (0.22)	$\begin{array}{c} 89 \rightarrow 5 \\ (-84) \end{array}$	$\begin{array}{c} 1 \rightarrow 88 \\ (87) \end{array}$	$3 \rightarrow 6 (3)$	$6 \rightarrow 0 (-6)$		
4d	254	13100	243	0.0807	$H-4 \to L (0.61)$	$\begin{array}{c} 90 \rightarrow 10 \\ (-80) \end{array}$	$\begin{array}{c} 9 \rightarrow 75 \\ (66) \end{array}$	$\begin{array}{c} 1 \rightarrow 13 \\ (12) \end{array}$	$0 \rightarrow 1 \ (1)$		
	289 (sh)	6600	329	0.0259	$H-1 \to L (0.93)$	$\begin{array}{c} 98 \rightarrow 5 \\ (-93) \end{array}$	$\begin{array}{c} 1 \rightarrow 87 \\ (86) \end{array}$	$0 \rightarrow 7 \ (7)$	$0 \rightarrow 0 \ (0)$		
4e	266	21500	246	0.1239	$H-3 \rightarrow L+2 (0.88)$	$4 \rightarrow 4 (0)$	$0 \rightarrow 0 \ (0)$	$1 \rightarrow 2 (1)$	$95 \rightarrow 93$ (-2)		
	299 (sh)	7400	329	0.0357	H-1 \rightarrow L (0.89)	$\begin{array}{c} 95 \rightarrow 5\\ (-90) \end{array}$	$\begin{array}{c} 2 \rightarrow 89 \\ (87) \end{array}$	$3 \rightarrow 5 (2)$	$0 \rightarrow 0 \ (0)$		
4f	254	14000	233	0.0371	H-6 → L (0.38), H-5 → L (0.24), H-3 → L+1 (0.12)	$78 \rightarrow 5$ (-73)	$\begin{array}{c} 10 \rightarrow 86 \\ (76) \end{array}$	$7 \rightarrow 8 (1)$	$6 \rightarrow 0 (-6)$		
	287 (sh)	8800	294	0.0283	H-3 \rightarrow L (0.43), H \rightarrow L+2 (0.16), H \rightarrow L+3 (0.10)	$\begin{array}{c} 97 \rightarrow 24 \\ (-73) \end{array}$	$\begin{array}{c} 1 \rightarrow 55\\ (54) \end{array}$	$\begin{array}{c} 2 \rightarrow 20 \\ (18) \end{array}$	$0 \rightarrow 1 \ (1)$		
	298 (sh)	6600	333	0.0361	$H-1 \to L (0.92)$	$\begin{array}{c} 95 \rightarrow 5 \\ (-90) \end{array}$	$\begin{array}{c} 2 \rightarrow 90 \\ (88) \end{array}$	$3 \rightarrow 5 (2)$	$0 \rightarrow 0 \ (0)$		

^aObtained via TD-DFT utilizing the CAM-B3LYP functional. ^bChanges in the wave function amplitude with transition for the optical electron.



Figure 7. Molecular orbital diagrams for complex **4a**. Orbitals on the left-hand side are the major MOs involved in the 286 nm transition, while orbitals on the right-hand side show the major contributors to the 251 nm transition.



Figure 8. Molecular orbital diagrams for the transition at 302 nm in complex 4b.

achieved because the polarization or asymmetry of the acceptor MO preferentially enhances bands associated with the LUMO. For example analysis of the nature of the enhanced Raman bands³⁶ has been previously used to establish that the MLCT



Figure 9. Resonance Raman spectra of 4b and c obtained in CH_3CN at 10^{-3} M concentrations using 350.7 nm excitation.

transition of $[Ru(pypz)_3]^{2+}$ (where pypz is 2-(2-pyridyl)pyrazine) is polarized to the pyrazine, as evidenced by the enhancement of pyrazine over pyridine bands in the resonance Raman spectrum.³⁷ In a study of Re(CO)₃Cl(dppz-11-CO₂Et) (dppz is dipyrido[3,2-*a*:2',3'-*c*]phenazine) the enhancement of the ester C=O band was indicative of an MLCT state with delocalized ligand π^* character³⁸—the unsubstituted ligand shows enhancement of only the phen-based modes due to the localized electronic structure present in dppz complexes.³⁹

The bands that show enhancement in the resonance Raman spectrum of **4b** are based on the triazole and 4-nitrophenyl moieties. This is consistent with the nature of the probed transition, shown in Figure 8. The modes at 854, 976, 1111, 1349, and 1490 cm⁻¹ are all of this nature, and Figure 10a shows the band at 1349 cm⁻¹ as an example. Along with these modes the band at 2032 cm⁻¹ is a carbonyl stretch and that at 1612 cm⁻¹ is more pyridine based (Figure 10b).



Figure 10. Vibrational mode diagrams of complex 4b showing (a) the mode at 1349 cm^{-1} and (b) the mode at 1612 cm^{-1} .

Despite the poor enhancement seen in the resonance Raman spectrum of 4c, we observe a carbonyl stretch at 2035 cm⁻¹, confirming the MLCT nature of the electronic transition. The other bands at 976, 1032, 1180, 1256, 1314, 1564, and 1620 cm⁻¹ are characterized as delocalized over the ligand and R group and as such are less informative as to the nature of the acceptor MO. In view of the poor resonance from the lower energy transitions for these samples at this excitation wavelength, preresonance Raman cannot be discounted. This would enhance modes that mimic the strong UV transitions which are π - π * in nature, enhancement of delocalised modes is not inconsistent with this finding.

Excited State Spectroscopy. Table 3 includes the emission data for 4a,c-f. Complex 4b, the 4-nitrophenyl-

Table 3. Emission Maxima, Obtained in CH₃CN at 350.7 nm Excitation, and Emission Lifetimes, Obtained in CH₃CN at 354.7 nm, of 4a,c-f at Room Temperature

complex	$\lambda_{\rm em}/{\rm nm}$	$\tau_{\rm em}{}^a/{ m ns}$	$\Phi \times 10^{-4}$	$k_{\rm r} \times 10^4 / {\rm s}^{-1}$	$k_{\rm nr} \times 10^7$
4a	538	15	4.3	2.8	7.7
4c	419	10	1.3	1.3	10.0
	524	13	1.3	1.0	7.7
4d	537	17	2.0	1.2	5.9
4e	526	13	2.1	1.6	7.7
4f	520	13	8.3	6.4	7.7
$^{a}\pm 10\%$.					

substituted species, does not show any emission, which is consistent with the significantly shorter lifetimes observed for analogous 4-nitrophenyl-substituted complexes based on the ligand 2.²² The emission band shows very little change with differing R group, with λ_{em} falling between 520 and 538 nm. 4c also displays a second emission band at 419 nm. Lifetimes are very short, between 10 and 17 ns, and do not appear to be significantly affected by substituent. Finally, the quantum yields of 4a,c-f are extremely weak, in the range $(1.3-8.3) \times 10^{-4}$. These quantum yields are 2 orders of magnitude lower than those of the 2-based analogues²² and 1 order of magnitude less than those of the 2-based tridentate analogues.²⁰ Despite the modest quantum yields of all complexes reported here, we do observe that the material with the bulkiest group (4f) exhibits the greatest quantum yield, which is not inconsistent with the literature.17

The observed fluorescence quantum yields and lifetimes are smaller than those for analogous complexes based on the 2 ligand.²² This is consistent with a study performed by Thummel et al.⁴⁰ on a series of 2-(2'-pyridyl)indoles incorporating 3,3'-methylene, 3,3'-dimethylene, 3,3'-trimethylene, and 3,3'-tetramethylene groups. It was reported that, as the length of the 3,3'-group increases, the extra flexibility correlates to a decrease in quantum yield and excited-state lifetime. This is the same trend observed for complexes with the ligand 2 in comparison to the more flexible ligand of type 4.¹¹

Electrochemistry. The electrochemistry of the rhenium compounds 4a-f in CH₂Cl₂ solution was probed with cyclic voltammetry using Bu₄NPF₆ as supporting electrolyte. Data are presented in Table 4 and a representative voltammogram, that of 4a, in Figure 11. An internal decamethylferrocene $(Fc^*)^{+/0}$ reference standard was used, under which conditions $E^{\circ}([FcH]^{+/0}) = 0.55 \text{ V.}^{41}$ At first glance the electrochemical behavior of 4a-f resembles that of the rhenium triazoles previously reported by this group²² with Re oxidation and ligand reduction processes at opposite extremes of the solvent window. Closer examination, however, reveals a key difference for 4a-e. For these samples the Re^{I}/Re^{II} couple now gives rise to a quasi-reversible feature at ca. 1.5 V. Variation of E° with differing triazole ligand substituents are within or close to the experimental error. The literature contains many reports of the electrochemistry of rhenium tricarbonyl diimine halide complexes.^{3,7,42} This previous work, however, has concentrated on systems in which the ligand generates a five-membered Rechelate ring, and for the most part⁴³ these characteristically display an irreversible Re^I/Re^{II} oxidation. The increased reversibility we observe for this process in 4a-e is presumably the result of greater stabilization of the ReII oxidation state provided by the six-membered chelate ring, although electronic effects may play some part. The six-membered ring

Table 4. Electrochemical Data for $4a-f^a$

compd	$E_{\rm pc}({\rm triazole})/{\rm V}$	$E_{\rm pc}({\rm nitrobenzene})/{\rm V}$	$E^{\circ}(nitrobenzene)/V$	$E^{\circ}(\text{Re})/\text{V}$
4a	-1.75			1.50
4b		-1.63	-0.94	1.54
4c	-1.74			1.49
4d	-1.77			1.50
4e	-1.70			1.54
4f	-1.75			$1.54 (E_{\rm pa})$
3b		-1.7	-0.97	

^aConditions: 1×10^{-3} M in CH₂Cl₂ solution, 0.1 M Bu₄NPF₆, referenced with internal $[Fc^*]^{+/0} = 0.00$ V.



Figure 11. Cyclic voltammogram for **4a** at 100 mV s⁻¹ (1×10^{-3} M in CH₂Cl₂ solution, 0.1 M Bu₄NPF₆, window referenced with equimolar [Fc*]^{+/0}).

configuration is uncommon but, where reported, gives rise to a similar quasi-reversible Re^I/Re^{II} feature.⁴⁴ Why the steroid analogue **4f** should behave differently and exhibit an irreversible Re oxidation process is unknown, but this could be connected to the presence of the OH functionality in the substituent.

The cathodic electrochemistry is similar to that of the rhenium triazole systems previously presented.²² With the exception of the nitro-substituted compound **4b**, the voltammograms of the diimine complexes are characterized by an irreversible ligand-based reduction wave. This occurs at ca. -1.7 V, and the reversibility does not improve with increased scan rate. Variations of $E_{\rm pc}$ with the differing triazole ligand substituents are within or close to the experimental error.

The reduction scan of the nitro-substituted compound **4b** closely resembles that of the uncoordinated ligand (**3b**, Table 4) and those of nitrobenzyl and nitrophenyl compounds we have previously reported.²² The triazole reduction process falls outside the swept potential range. Observed instead is electrochemical behavior characteristic of the nitrobenzene fragment,⁴⁵ a reversible one-electron reduction to a stable radical anion, followed by irreversible processes.

CONCLUSIONS

A series of electronically tuned fac-Re(CO)₃Cl inverse pyridyl-1,2,3-triazole complexes have been synthesized in good to excellent yields (72-95%) by refluxing methanol solutions of [Re(CO)₅Cl] and the substituted [2-(4-R-1H-1,2,3-triazol-1yl)methyl]pyridine ligands (py(CH₂)tri-R). The resulting rhenium(I) complexes were characterized by elemental analysis, HR-ESI-MS, and IR and ¹H and ¹³C NMR spectroscopy. Additionally, the molecular structures of three of the complexes were confirmed using X-ray crystallography. A systematic spectroscopic and computational study of the family of complexes 4a-f gave information on their electronic structure. It was found that the lowest energy transition is MLCT in nature, with the acceptor orbitals being located on the pyridine section of the ligand; consistent with this polarization of charge, the substituents appear to have little effect on the electronic properties. Furthermore, except in the case of the nitro complex

4b, the effect of changing the -R group was found to be minimal with respect to the absorption spectra and emission maxima and the electrochemical oxidation and reduction processes. This indicates that, similarly to complexes with ligand 2, the 1,2,3-triazolyl unit acts as an insulating unit. The compounds are weakly emissive, with short lifetimes (τ < 20 ns) in solution at room temperature. This behavior is consistent with the greater flexibility in the ligand that facilitates nonradiative decay. The functional group tolerance of the CuAAC methodology used to generate the bidentate [2-(4-R-1H-1,2,3-triazol-1-yl)methyl]pyridine "click" ligands should enable a wide range of functionalized complexes to be readily synthesized without affecting the intrinsic photophysical properties of the complexes. This property could potentially be useful in tuning the solubility of new optical materials without altering the electronic properties.

EXPERIMENTAL SECTION

Unless otherwise stated, all reagents were purchased from commercial sources and used without further purification. Petrol refers to the fraction of petroleum ether boiling in the range 40-60 °C. Reactions were followed by TLC on aluminum-backed silica gel 60 F254 sheets from E. Merck, visualized under UV light. Column chromatography was performed using Scharlau silica gel 60, 0.04-0.06 mm, 230-400 mesh. All melting points were determined using a Sanyo Gallenkamp apparatus and are uncorrected. ¹H and ¹³C NMR spectra were recorded on either a 400 MHz Varian 400 MR or a Varian 500 MHz VNMRS spectrometer at 298 K. Chemical shifts are reported in parts per million and referenced to residual solvent peaks (CDCl₃, ${}^{1}\text{H} \delta 7.26$ ppm, ¹³C δ 77.16 ppm; d₆-acetone, ¹H 2.05 ppm, ¹³C 29.84, 206.26 ppm; CD₃CN, ¹H δ 1.94 ppm, ¹³C δ 1.32, 118.26 ppm; *d*₆-DMSO, ¹H 2.50 ppm, ¹³C 35.52 ppm). Despite extended acquisition times, it was not possible to observe the carbonyl carbon peaks in the ¹³C NMR spectra. Coupling constants (J) are reported in hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: m = multiplet, quint = quintet, q = quartet, t = triplet, d = doublet, s = singlet, br = broad. IR spectra were recorded on a Bruker ALPHA FT-IR spectrometer with an attached ALPHA-P ATR measurement module. Microanalyses were performed at the Campbell Microanalytical Laboratory at the University of Otago. Electrospray mass spectra (ESI-MS) were collected on a Bruker micro-TOF-Q spectrometer. UV-visible absorption spectra were acquired with a Perkin-Elmer Lambda-950 spectrophotometer or Jasco V-550 spectrophotometer. Cyclic voltammetric experiments in CH₂Cl₂ were performed at 20 °C on solutions degassed with argon. A threeelectrode cell was used with Cypress Systems 1.4 mm diameter glassycarbon working, Ag/AgCl reference, and platinum-wire auxiliary electrodes. The solution was $\sim 10^{-3}$ M in electroactive material and contained 0.1 M Bu₄NPF₆ as the supporting electrolyte. Voltammograms were recorded with the aid of a Powerlab/4sp computercontrolled potentiostat. Potentials are referenced to the reversible formal potential (taken as $E^{\circ} = 0.00$ V) for the decamethylferrocene $[Fc^*]^{+/0}$ process.⁴⁶ Under the same conditions, E° calculated for $[FcH]^{+/0}$ was 0.55 V.⁴¹ The ligands 3a,²⁶ 3d,²⁶ and 3f²⁴ were prepared using our previously reported methods. 2-Propyn-1-ylxanthine was prepared using the reported literature method.

General Synthetic Procedure for the Re(I) Complexes. [Re(CO)₅Cl] (1.0 equiv) and one of the ligands 3a-f (1.0 equiv) were dissolved in methanol (30–50 mL) and heated at reflux for 16 h. The volume of solvent was reduced by half using rotary evaporation, and then the solution was cooled to 4 °C in the refrigerator for 16 h. The resulting colorless solid was isolated by filtration and washed with petroleum ether to give the complexes 4a-f (72–95%).

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ASSOCIATED CONTENT

S Supporting Information

Text, figures, tables, and CIF files giving full experimental descriptions, spectroscopic data, and crystallographic data for **4a,d,e**. This material is available free of charge via the Internet at http://pubs.acs.org. The crystallographic data are also available from the Cambridge Crystallographic Database as file nos. CCDC 886282–886284.

AUTHOR INFORMATION

Corresponding Author

*E-mail: jcrowley@chemistry.otago.ac.nz. Fax: +64 3 479 7906. Tel: +64 3 479 7731.

Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Wrighton, M.; Morse, D. L. J. Am. Chem. Soc. 1974, 96, 998–1003.

(2) Kumar, A.; Sun, S.-S.; Lees, A. Photophysics and Photochemistry of Organometallic Rhenium Diimine Complexes. In *Photophysics of Organometallics*; Lees, A. J., Ed.; Springer: Berlin/Heidelberg, 2010; Topics in Organometallic Chemistry Vol. 29, pp 37–71. Uppal, B. S.; Booth, R. K.; Ali, N.; Lockwood, C.; Rice, C. R.; Elliott, P. I. P. *Dalton Trans.* **2011**, *40*, 7610–7616. Werrett, M. V.; Chartrand, D.; Gale, J. D.; Hanan, G. S.; MacLellan, J. G.; Massi, M.; Muzzioli, S.; Raiteri, P.; Skelton, B. W.; Silberstein, M.; Stagni, S. *Inorg. Chem.* **2011**, *50*, 1229–1241. Mbagu, M. K.; Kebulu, D. N.; Winstead, A.; Pramanik, S. K.; Banerjee, H. N.; Iwunze, M. O.; Wachira, J. M.; Greco, G. E.; Haynes, G. K.; Sehmer, A.; Sarkar, F. H.; Ho, D. M.; Pike, R. D.; Mandal, S. K. *Inorg. Chem. Commun.* **2012**, *21*, 35–38.

(3) Fraser, M. G.; Clark, C. A.; Horvath, R.; Lind, S. J.; Blackman, A. G.; Sun, X. Z.; George, M. W.; Gordon, K. C. *Inorg. Chem.* **2011**, *50*, 6093–6106.

(4) Ranjan, S.; Lin, S.-Y.; Hwang, K.-C.; Chi, Y.; Ching, W.-L.; Liu, C.-S.; Tao, Y.-T.; Chien, C.-H.; Peng, S.-M.; Lee, G.-H. Inorg. Chem. **2003**, 42, 1248–1255. Lundin, N. J.; Blackman, A. G.; Gordon, K. C.; Officer, D. L. Angew. Chem., Int. Ed. **2006**, 45, 2582–2584. Walsh, P. J.; Lundin, N. J.; Gordon, K. C.; Kim, J.-Y.; Lee, C.-H. Opt. Mat. **2009**, 31, 1525–1531. Mizoguchi, S. K.; Santos, G.; Andrade, A. M.; Fonseca, F. J.; Pereira, L.; Murakami Iha, N. Y. Synth. Met. **2011**, 161, 1972–1975. Cleland, D. M.; Irwin, G.; Wagner, P.; Officer, D. L.; Gordon, K. C. Chem. Eur. J. **2009**, 15, 3682–3690.

(5) Yedukondalu, M.; Ravikanth, M. J. Chem. Sci. 2011, 123, 201– 214. McLean, T. M.; Moody, J. L.; Waterland, M. R.; Telfer, S. G. Inorg. Chem. 2012, 51, 446–455. Yi, X.; Zhao, J.; Wu, W.; Huang, D.; Ji, S.; Sun, J. Dalton Trans. 2012, 41, 8931–8940.

(6) Takeda, H.; Koike, K.; Morimoto, T.; Inumaru, H.; Ishitani, O. Adv. Inorg. Chem. 2011, 63, 137–186. Takeda, H.; Ishitani, O. Coord. Chem. Rev. 2010, 254, 346–354. Coleman, A.; Brennan, C.; Vos, J. G.; Pryce, M. T. Coord. Chem. Rev. 2008, 252, 2585–2595. Tamaki, Y.; Watanabe, K.; Koike, K.; Inoue, H.; Morimoto, T.; Ishitani, O. Faraday Discuss. 2012, 155. Schneider, J.; Jia, H.; Muckerman, J. T.; Fujita, E. Chem. Soc. Rev. 2012, 41, 2036–2051. Bruckmeier, C.; Lehenmeier, M. W.; Reithmeier, R.; Rieger, B.; Herranz, J.; Kavakli, C. Dalton Trans. 2012, 41, 5026–5037. Bian, Z.-Y.; Wang, H.; Fu, W.-F.; Li, L.; Ding,

A.-Z. Polyhedron 2012, 32, 78–85. Agarwal, J.; Fujita, E.; Schaefer, H. F.; Muckerman, J. T. J. Am. Chem. Soc. 2012, 134, 5180–5186. Schneider, J.; Vuong, K. Q.; Calladine, J. A.; Sun, X.-Z.; Whitwood, A. C.; George, M. W.; Perutz, R. N. Inorg. Chem. 2011, 50, 11877–11889. Koike, K.; Naito, S.; Sato, S.; Tamaki, Y.; Ishitani, O. J. Photochem. Photobiol., A 2009, 207, 109–114.

(7) Smieja, J. M.; Kubiak, C. P. Inorg. Chem. 2010, 49, 9283–9289.
(8) Chakrabarty, R.; Mukherjee, P. S.; Stang, P. J. Chem. Rev. 2011, 111, 6810–6918. Kumar, A.; Sun, S.-S.; Lees, A. J. Coord. Chem. Rev. 2008, 252, 922–939. Lee, S. J.; Hupp, J. T. Coord. Chem. Rev. 2006, 250, 1710–1723. Hupp, J. T. Struct. Bonding (Berlin) 2006, 121, 145–165. Dinolfo, P. H.; Hupp, J. T. Chem. Mater. 2001, 13, 3113–3125.
(9) Lo, K. K.-W.; Choi, A. W.-T.; Law, W. H.-T. Dalton Trans. 2012, 41, 6021–6047. Baggaley, E.; Weinstein, J. A.; Williams, J. A. G. Coord. Chem. Rev. 2012, 256, 1762–1785. Lo, K. K.-W.; Zhang, K. Y.; Li, S. P.-Y. Eur. J. Inorg. Chem. 2011, 2011, 3551–3568. Balasingham, R. G.; Coogan, M. P.; Thorp-Greenwood, F. L. Dalton Trans. 2011, 40, 11663–11674.

(10) Das, S.; Panda, B. K. Polyhedron 2006, 25, 2289–2294. Wang, K.; Huang, L.; Gao, L.; Jin, L.; Huang, C. Inorg. Chem. 2002, 41, 3353–3358. Shavaleev, N. M.; Barbieri, A.; Bell, Z. R.; Ward, M. D.; Barigelletti, F. New J. Chem. 2004, 28, 398–405.

(11) Li, X.-W.; Li, H.-Y.; Wang, G.-F.; Chen, F.; Li, Y.-Z.; Chen, X.-T.; Zheng, Y.-X.; Xue, Z.-L. *Organometallics* **2012**, *31*, 3829–3835.

(12) Crowley, J. D.; McMorran, D. A. Top. Heterocycl. Chem. 2012, 28, 31–84. Schweinfurth, D.; Deibel, N.; Weisser, F.; Sarkar, B. Nachr. Chem. 2011, 59, 937–941. Struthers, H.; Mindt, T. L.; Schibli, R. Dalton Trans. 2010, 39, 675–696.

(13) Hein, J. E.; Fokin, V. V. *Chem. Soc. Rev.* **2010**, *39*, 1302–1315. Meldal, M.; Tornoe, C. W. *Chem. Rev.* **2008**, *108*, 2952–3015. Wu, P.; Fokin, V. V. *Aldrichim. Acta* **2007**, *40*, 7–17.

(14) Guha, P. M.; Phan, H.; Kinyon, J. S.; Brotherton, W. S.; Sreenath, K.; Simmons, J. T.; Wang, Z.; Clark, R. J.; Dalal, N. S.; Shatruk, M.; Zhu, L. *Inorg. Chem.* **2012**, *51*, 3465–3477.

(15) Schweinfurth, D.; Pattacini, R.; Strobel, S.; Sarkar, B. Dalton Trans. 2009, 9291–9297.

(16) Felici, M.; Contreras-Carballada, P.; Smits, J. M. M.; Nolte, R. J. M.; Williams, R. M.; De Cola, L.; Feiters, M. C. Molecules 2010, 15, 2039-2059. Zanarini, S.; Felici, M.; Valenti, G.; Marcaccio, M.; Prodi, L.; Bonacchi, S.; Contreras-Carballada, P.; Williams, R. M.; Feiters, M. C.; Nolte, R. J. M.; De Cola, L.; Paolucci, F. Chem. Eur. J. 2011, 17, 4640-4647 (S4640/1-S4640/4). Stengel, I.; Mishra, A.; Pootrakulchote, N.; Moon, S.-J.; Zakeeruddin, S. M.; Graetzel, M.; Baeuerle, P. J. Mater. Chem. 2011, 21, 3726-3734. Liu, S.; Müller, P.; Takase, M. K.; Swager, T. M. Inorg. Chem. 2011, 50, 7598-7609. Happ, B.; Escudero, D.; Hager, M. D.; Friebe, C.; Winter, A.; Gorls, H.; Altuntas, E.; Gonzalez, L.; Schubert, U. S. J. Org. Chem. 2010, 75, 4025-4038. Happ, B.; Friebe, C.; Winter, A.; Hager, M. D.; Hoogenboom, R.; Schubert, U. S. Chem. Asian J. 2009, 4, 154-163. Fletcher, J. T.; Bumgarner, B. J.; Engels, N. D.; Skoglund, D. A. Organometallics 2008, 27, 5430-5433. Juricek, M.; Felici, M.; Contreras-Carballada, P.; Lauko, J.; Bou, S. R.; Kouwer, P. H. J.; Brouwer, A. M.; Rowan, A. E. J. Mater. Chem. 2011, 21, 2104-2111. Juricek, M.; Kouwer, P. H. J.; Rowan, A. E. Chem. Commun. 2011, 47, 8740-8749. Sykes, D.; Ward, M. D. Chem. Commun. 2011, 47, 2279-2281

(17) Felici, M.; Contreras-Carballada, P.; Vida, Y.; Smits, J. M. M.; Nolte, R. J. M.; De Cola, L.; Williams, R. M.; Feiters, M. C. *Chem. Eur. J.* **2009**, *15*, 13124–13134.

(18) Zhang, G.; Wang, Y.; Wen, X.; Ding, C.; Li, Y. Chem. Commun. 2012, 48, 2979–2981. Amadio, E.; Bertoldini, M.; Scrivanti, A.; Chessa, G.; Beghetto, V.; Matteoli, U.; Bertani, R.; Dolmella, A. Inorg. Chim. Acta 2011, 370, 388–393. D'Amora, A.; Fanfoni, L.; Cozzula, D.; Guidolin, N.; Zangrando, E.; Felluga, F.; Gladiali, S.; Benedetti, F.; Milani, B. Organometallics 2010, 29, 4472–4485.

(19) Urankar, D.; Pevec, A.; Kosmrlj, J. *Eur. J. Inorg. Chem.* 2011, 1921–1929. Bratsos, I.; Urankar, D.; Zangrando, E.; Genova-Kalou, P.; Kosmrlj, J.; Alessio, E.; Turel, I. *Dalton Trans.* 2011, 40, 5188–5199.

Organometallics

(20) Anderson, C. B.; Elliott, A. B. S.; Lewis, J. E. M.; McAdam, C. J.; Gordon, K. C.; Crowley, J. D. *Dalton Trans.* **2012**, *41*, 14625–14632.

(21) Obata, M.; Kitamura, A.; Mori, A.; Kameyama, C.; Czaplewska, J. A.; Tanaka, R.; Kinoshita, I.; Kusumoto, T.; Hashimoto, H.; Harada, M.; Mikata, Y.; Funabiki, T.; Yano, S. *Dalton Trans.* **2008**, 3292–3300. Boulay, A.; Seridi, A.; Zedde, C.; Ladeira, S.; Picard, C.; Maron, L.; Benoist, E. *Eur. J. Inorg. Chem.* **2010**, 5058–5062. Seridi, A.; Wolff, M.; Boulay, A.; Saffon, N.; Coulais, Y.; Picard, C.; Machura, B.; Benoist, E. *Inorg. Chem. Commun.* **2011**, *14*, 238–242. Clede, S.; Lambert, F.; Sandt, C.; Gueroui, Z.; Refregiers, M.; Plamont, M.-A.; Dumas, P.; Vessieres, A.; Policar, C. *Chem. Commun.* **2012**, *48*, 7729–7731.

(22) Kim, T. Y.; Elliott, A. B. S.; Shaffer, K. J.; John McAdam, C.; Gordon, K. C.; Crowley, J. D. *Polyhedron* **2012**, DOI: 10.1016/ j.poly.2012.05.003.

(23) Feldman, A. K.; Colasson, B.; Fokin, V. V. Org. Lett. 2004, 6, 3897–3899.

(24) Kilpin, K. J.; Gavey, E. L.; McAdam, C. J.; Anderson, C. B.; Lind, S. J.; Keep, C. C.; Gordon, K. C.; Crowley, J. D. *Inorg. Chem.* **2011**, *50*, 6334–6346.

(25) Gower, M. L.; Crowley, J. D. Dalton Trans. 2010, 39, 2371–2378. Crowley, J. D.; Gavey, E. L. Dalton Trans. 2010, 39, 4035–4037. Crowley, J. D.; Bandeen, P. H. Dalton Trans. 2010, 39, 612–623.

(26) Crowley, J. D.; Bandeen, P. H.; Hanton, L. R. Polyhedron 2010, 29, 70-83.

(27) Zhu and co-workers have previously reported the synthesis of **3b,c** using a different method; see: Kuang, G.-C.; Guha, P. M.; Brotherton, W. S.; Simmons, J. T.; Stankee, L. A.; Nguyen, B. T.; Clark, R. J.; Zhu, L. J. Am. Chem. Soc. **2011**, 133, 13984–14001. Kuang, G.-C.; Michaels, H. A.; Simmons, J. T.; Clark, R. J.; Zhu, L. J. Org. Chem. **2010**, 75, 6540–6548. Brotherton, W. S.; Michaels, H. A.; Simmons, J. T.; Clark, R. J.; Clark, R. J.; Clark, R. J.; Zhu, L. J. Org. Chem. **2010**, 75, 6540–6548. Brotherton, W. S.; Michaels, H. A.; Simmons, J. T.; Clark, R. J.; Clark, R. J.; Dalal, N. S.; Zhu, L. Org. Lett. **2009**, 11, 4954–4957.

(28) Záliš, S.; Consani, C.; Nahhas, A. E.; Cannizzo, A.; Chergui, M.; Hartl, F.; Vlček, A., Jr. *Inorg. Chim. Acta* **2011**, *374*, *578*–585. Takeda, H.; Koike, K.; Inoue, H.; Ishitani, O. J. Am. Chem. Soc. **2008**, *130*, 2023–2031. Hayashi, Y.; Kita, S.; Brunschwig, B. S.; Fujita, E. J. Am. Chem. Soc. **2003**, *125*, 11976–11987.

(29) Fleischel, O.; Wu, N.; Petitjean, A. Chem. Commun. 2010, 46, 8454–8456.

(30) Kilpin, K. J.; Crowley, J. D. *Polyhedron* **2010**, *29*, 3111–3117. (31) Urankar, D.; Pinter, B.; Pevec, A.; De Proft, F.; Turel, I.; Kosmrlj, J. *Inorg. Chem.* **2010**, *49*, 4820–4829.

(32) Lundin, N. J.; Walsh, P. J.; Howell, S. L.; Blackman, A. G.; Gordon, K. C. *Chem. Eur. J.* **2008**, *14*, 11573–11583. Howell, S. L.; Gordon, K. C.; Waterland, M. R.; Leung, K. H.; Phillips, D. L. *J. Phys. Chem. A* **2006**, *110*, 11194–11199. Howell, S. L.; Matthewson, B. J.; Polson, M. I. J.; Burrell, A. K.; Gordon, K. C. *Inorg. Chem.* **2004**, *43*, 2876–2887. Howell, S. L.; Gordon, K. C. *J. Phys. Chem. A* **2004**, *108*, 2536–2544.

(33) Elliott, A. B. S.; Horvath, R.; Gordon, K. C. Chem. Soc. Rev. 2012, 41, 1929–1946.

(34) Horvath, R.; Otter, C. A.; Gordon, K. C.; Brodie, A. M.;
Ainscough, E. W. Inorg. Chem. 2010, 49, 4073-4083. Horvath, R.;
Gordon, K. C. Coord. Chem. Rev. 2010, 254, 2505-2518. Lind, S. J.;
Walsh, T. J.; Blackman, A. G.; Polson, M. I. J.; Irwin, G. I. S.; Gordon, K. C. J. Phys. Chem. A 2009, 113, 3566-3575. Earles, J. C.; Gordon, K. C.;
Officer, D. L.; Wagner, P. J. Phys. Chem. A 2007, 111, 7171-7180.
(35) Fraser, M. G.; Blackman, A. G.; Irwin, G. I. S.; Easton, C. P.;
Gordon, K. C. Inorg. Chem. 2010, 49, 5180-5189. Lind, S. J.; Gordon, K. C.;
Gambhir, S.; Officer, D. L. Phys. Chem. Chem. Phys. 2009, 11, 5598-5607. Walsh, P. J.; Gordon, K. C.; Wagner, P.; Officer, D. L. ChemPhysChem 2006, 7, 2358-2365. Clark, R. J. H.; Dines, T. J. Angew. Chem., Int. Ed. 1986, 25, 131-158. Hirakawa, A. Y.; Tsuboi, M. Science 1975, 188, 359-361.

(36) Treffertziemelis, S. M.; Golus, J.; Strommen, D. P.; Kincaid, J. R. *Inorg. Chem.* **1993**, *32*, 3890–3894. Treffertziemelis, S. M.; Kincaid, J. R. J. Raman Spectrosc. **1994**, *25*, 893–897. (37) Danzer, G. D.; Golus, J. A.; Kincaid, J. R. J. Am. Chem. Soc. **1993**, 115, 8643–8648.

(38) Walsh, P. J.; Gordon, K. C.; Lundin, N. J.; Blackman, A. G. J. Phys. Chem. A 2005, 109, 5933–5942.

(39) Horvath, R.; Gordon, K. C. *Inorg. Chim. Acta* **2011**, 374, 10–18. Fees, J.; Kaim, W.; Moscherosch, M.; Matheis, W.; Klima, J.; Krejcik, M.; Zalis, S. *Inorg. Chem.* **1993**, 32, 166–174.

(40) Herbich, J.; Rettig, W.; Thummel, R. P.; Waluk, J. Chem. Phys. Lett. 1992, 195, 556-562.

(41) Barriere, F.; Geiger, W. E. J. Am. Chem. Soc. 2006, 128, 3980-3989.

(42) Liu, X.; Xia, H.; Gao, W.; Wu, Q.; Fan, X.; Mu, Y.; Ma, C. J. Mater. Chem. 2012, 22, 3485–3492. Roy, S.; Kubiak, C. P. Dalton Trans. 2010, 39, 10937–10943. Klein, A.; Vogler, C.; Kaim, W. Organometallics 1996, 15, 236–244.

(43) Drozdz, A.; Bubrin, M.; Fiedler, J.; Zalis, S.; Kaim, W. Dalton Trans. 2012, 41, 1013-1019.

(44) Chen, Y.; Liu, W.; Jin, J.-S.; Liu, B.; Zou, Z.-G.; Zuo, J.-L.; You, X.-Z. J. Organomet. Chem. **2009**, 694, 763–770.

(45) Smith, W. H.; Bard, A. J. J. Am. Chem. Soc. 1975, 97, 5203–5210. Silvester, D. S.; Wain, A. J.; Aldous, L.; Hardacre, C.; Compton, R. G. J. Electroanal. Chem. 2006, 596, 131–140.

(46) Noviandri, I.; Brown, K. N.; Fleming, D. S.; Gulyas, P. T.; Lay,
 P. A.; Masters, A. F.; Phillips, L. J. Phys. Chem. B 1999, 103, 6713–

6722. (47) Daly, J. W.; Padgett, W. L.; Shamim, M. T. J. Med. Chem. 1986,

(47) Daly, J. W.; Padgett, W. L.; Shamim, M. T. J. Med. Chem. 1986, 29, 1305–1308.