Inorganic Chemistry
Article
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cis-1,3,5-Triaminocyclohexane as a Facially Capping Ligand for Ruthenium(II)

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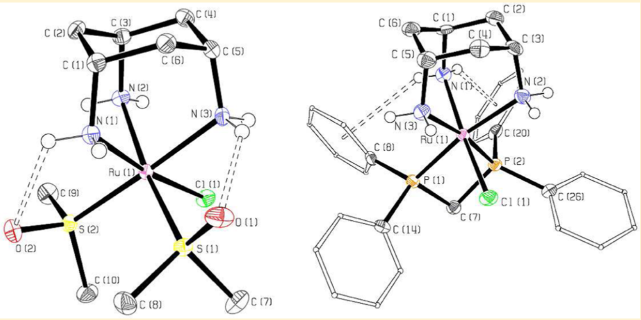
Supporting Information



ABSTRACT: Reaction of *cis*-[RuCl$_2$(DMSO-*S*)$_3$(DMSO-*O*)] with *cis*-1,3,5-triaminocyclohexane (tach) results in the formation of [RuCl(tach)(DMSO-*S*)$_2$]Cl, a valuable precursor for a wide range of other tach-containing Ru complexes. Reaction of [RuCl(tach)(DMSO-*S*)$_2$]Cl with the chelating nitrogen-based ligands (N−N = bipyridine, phenanthroline, and ethylenediamine) affords [Ru(N−N)(DMSO-*S*)$_2$(tach)][Cl]$_2$. A similar reaction between [RuCl(tach)(DMSO-*S*)]Cl with the chelating phosphorus-based ligands (P−P = dppm, dppe, dppp, dppb, dppv, and dppben) leads to the formation of [RuCl(P−P)(tach)]Cl. The structures of 10 examples of the tach-containing complexes have been determined by single crystal X-ray diffraction. An examination of the structural metrics obtained from these studies indicates that the tach ligand is a strong sigma donor. In addition, the presence of the NH$_2$ groups in the tach ligand allow for participation in hydrogen bonding further modulating the coordinative properties of the ligand.

INTRODUCTION

Ruthenium half-sandwich compounds[1] find applications in a diverse range of fields including catalysis,[2] nonlinear optics,[3] and medical chemistry.[4] In this context, complexes of the general type [Ru(*fac*)L$_3$], where *fac* represents a general facially capping six-electron donor ligand, are of particular interest as the nature of the *fac* group may be used to affect the steric and electronic properties of the metal. Most conspicuously, complexes containing the cyclopentadienyl ligand (and its derivatives) [Ru(η^5-C$_5$R$_5$)L$_3$] are widely used, especially since a number of easily prepared starting materials are available, such as [RuCl(η^5-C$_5$H$_5$)(PPh$_3$)$_2$].[5] In many cases the cyclopentadienyl ligand is essentially inert, whereas the remaining ligands may be labile, thus enabling, for example, carbon-carbon and carbon-heteroatom bond formation.[2] Notably the substituents on the cyclopentadienyl ring can profoundly affect the chemistry of these species. For example, in the parent cyclopentadienyl case complexes of the type [Ru(η^5-C$_5$R$_5$)L$_3$] almost uniformly obey the 18-electron rule,[6] whereas in the corresponding pentamethylcyclopentadienyl case it is possible to isolate stable 16-electron compounds such as [Ru(η^5-C$_5$Me$_5$)Cl(PCy$_3$)].[7]

Given the effect that the facially capping group has on a metal center, ligands other than Cp, such as arenes,[8] tris(pyrazolyl)borates,[9] tacn,[10] cyclotriphosphates[11] and [9]-aneS$_3$[12] have been employed by others to control the relative steric and electronic properties of ruthenium complexes. The effect of the capping group may be especially important as ruthenium half-sandwich compounds have found applications as catalysts of carbon−carbon bond formation[2] and recently in direct C−H functionalizaton reactions.[13]

Ruthenium complexes with a facially capping arene have been shown to have potential as new therapeutic agents for the treatment of cancer. Two leading classes of complex have been studied, RAPTA-C developed by Dyson contains an η^6-bound cymene ligand and the water-solubilizing PTA phosphine,[14] whereas a series of compounds prepared by Sadler and co-workers contains a range of arene-capping groups and a bidentate ethylenediamine ligand.[15] This theme has been developed further with different arene capping groups,[16] and with [9]aneS$_3$[17] and tacn ligands.[18]

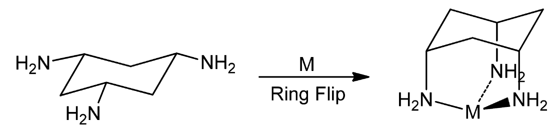
Although the nature of the facially capping ligand in ruthenium half sandwich compounds may be used primarily to control the steric and electronic properties of the metal, there are fewer examples where this ligand may be involved in secondary interactions, such as hydrogen bonding. This is important in the light of the discovery by Sadler et al. that NH$_2$ groups in an ethylenediamine ligand within an arene hand-sandwich complex assist in the binding of the metal to DNA.[19]

cis-1,3,5-Triaminocyclohexane (tach) is a ligand which has previously been used widely in the complexation of first row transition metal complexes.[20] Tach has a number of important features, first, following a ring “flip” from the all-equatorial position tach can adopt an all-axial conformation and thus present the three amino groups to a metal and act as a facially capping ligand (Scheme 1). In addition the three NH$_2$ groups also have the potential to act as hydrogen bond donors, a feature which could potentially be exploited in catalysis or, as is the case for the ethylenediamine ligand in the complexes

Received: December 21, 2012
Published: March 22, 2013

dx.doi.org/10.1021/ic302819j | *Inorg. Chem.* 2013, 52, 4517−4527

Scheme 1



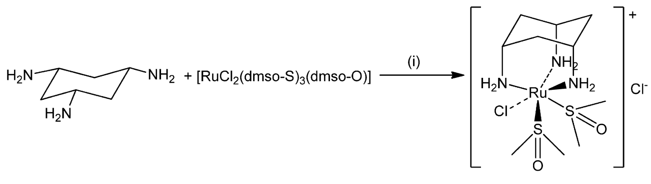
prepared by Sadler, may aid with the binding of the ruthenium complex to DNA.

With this in mind, we considered that tach could add a new dimension to the chemistry of ruthenium half-sandwich compounds. We report here the preparations of a range of tach-ruthenium complexes, which are rare examples of tach acting as a ligand to a metal outside the first row. We also characterize the complexes structurally and demonstrate that tach should be considered as a hard donor ligand under the HSAB classification.

■ RESULTS AND DISCUSSION

Treatment of a dimethylsulfoxide (DMSO) solution of *cis*-[RuCl$_2$(DMSO-*S*)$_3$(DMSO-*O*)] with tach followed by heating to 130 °C for 30 min gave a pale yellow solution from which [RuCl(DMSO-*S*)$_2$(κ^3-tach)]Cl, [**1**]Cl, could be isolated as a cream solid in excellent yield (Scheme 2). The ^{1}H NMR spectrum of [**1**]Cl recorded in D$_2$O solution exhibited resonances consistent with the proposed formulation, and notably the resonances for the tach ligand proved to be particularly diagnostic of the symmetry of the Ru complex. Six resonances were observed for the protons of the cyclohexyl ring and three resonances for the NH$_2$ groups of this ligand indicating local C_s symmetry at the metal. Furthermore, the absence of any axial−axial couplings between neighboring protons indicated that the ring had undergone the expected flip placing the amine groups in an equatorial position so that it may act in a facially capping manner. A singlet resonance of relative intensity 12 was observed at δ 3.36 for the methyl groups of the coordinated DMSO ligands. The IR spectrum of [**1**]Cl contained a band at 1061 cm^{-1} which was assigned to the S−O stretch of the DMSO ligands. In general, *O*-bound DMSO ligands exhibit stretches in the region 878−1035 cm^{-1}, whereas their *S*-bound analogues show bands between 1070 and 1233 cm^{-1}.[21] Given the fact that the band for the *S*-bound DMSO in [RuCl(η^5-C$_5$Me$_5$)(DMSO)$_2$] was observed at 1060 cm^{-1},[22] the same coordination mode for the DMSO was assigned in the case of [**1**]Cl. This was confirmed by single crystal X-ray diffraction.

Scheme 2[a]



cis-tach [1]Cl

[a](i) DMSO, 30 min, 130 °C.

Reaction of [**1**]Cl with KPF$_6$ allowed for exchange of the counter-anions and the formation of [**1**]PF$_6$. Slow evaporation of a methanol solution of this compound resulted in crystals of [**1**]PF$_6$ suitable for study by X-ray diffraction. Selected bond lengths and angles for [**1**]PF$_6$ are presented in Table 1, and details of the data collection and structure refinements for all complexes reported in this work are in Table 3.

The structure determination demonstrated that many of the structural features of [**1**]Cl, predicted from spectroscopic data, are also present in the solid state structure of [**1**]PF$_6$. As shown in Figure 1, the cationic unit [**1**]$^+$ contains a facially capping κ^3-bound tach ligand, and the remaining coordination sites on the metal are occupied by two *S*-bound DMSO ligands and a chloride. A complete discussion of the structural metrics for all the complexes reported with a view to ascertaining the properties of the tach ligand is provided later, but it is important to note the presence of both intra- [N(1)····O(2) 3.143(3) Å; N(3)····O(1) 2.852(3) Å;] and intermolecular [N(2)····O(1) 2.843(3) Å] hydrogen bonds between the NH$_2$ groups and the oxygen atoms of the DMSO groups.

To the best of our knowledge [**1**]Cl represents the first reported example of a ruthenium complex containing a facially capping tach ligand. In addition [**1**]Cl proved to be a versatile precursor for a number of other ruthenium complexes containing the tach ligand.

Reaction of an aqueous solution of [**1**]Cl with a slight excess of bidentate nitrogen-based ligands bipyridyl (bipy), phenanthroline (phen), or etheylenediamine (en) at 120 °C for 20 min gave red solutions from which complexes [Ru(DMSO-*S*)(κ^2-N-N)(κ^3-tach)][Cl]$_2$, (N−N = bipy [**2a**][Cl]$_2$, N−N = phen [**2b**]-[Cl]$_2$ N−N = en [**2c**][Cl]$_2$) could be isolated (Scheme 3). In a similar vein to complex [**1**]Cl, the resonances for the tach ligand in the ^{1}H NMR spectra of complexes [**2**]$^{2+}$ all indicated that the metal center possessed local C_s symmetry. Furthermore, in all three cases a singlet resonance of relative intensity six demonstrated the presence of single DMSO ligand. The structure of [**2a**][PF$_6$]$_2$, [**2b**][PF$_6$]$_2$·MeOH, and [**2c**][Cl][PF$_6$] were also confirmed by single crystal X-ray diffraction. The structures of the cations [**2a−c**]$^{2+}$ are presented in Figure 2.

The crystallographic determinations demonstrated that the dications [**2a**]$^{2+}$ and [**2b**]$^{2+}$ are essentially isostructural, with the tach ligand occupying three coordination sites, and the remaining positions around the metal being taken by either the bipy or the phen ligand and an *S*-bound DMSO. In both cases, the oxygen atom of the DMSO engages in a weak intramolecular hydrogen bonding with two NH$_2$-groups of the tach ligand (Figure 2). In the structure of [**2a**][PF$_6$]$_2$ stronger NH$_2$···O hydrogen bonds [N(1)···O(1) 2.996(4)Å] are observed between the neighboring molecules (Figure 3a) whereas the cationic units in [**2b**][PF$_6$]$_2$·MeOH form a dimer (Figure 3b) with the methanol-of-crystallization forming a hydrogen bonding bridge between the two ruthenium centers [N(3)···O(2) 2.951(2) Å, O(2)···O(1) 2.839(2) Å, N(3)···O(1) 3.127(3) Å]. In the case of complex [**2c**]$^{2+}$, despite two equivalents of NaPF$_6$ being added, the structure determined by single crystal X-ray diffraction indicated that only a single chloride counteranion had been replaced. Furthermore, in this structure each chloride anion is involved in weak hydrogen bonding with N−H groups of two ruthenium dications (Figure 3c) [N(1)···Cl(1) 3.277(1) Å, N(4)···Cl(1) 3.259(2) Å].

The ability of [**1**]Cl to act as a precursor for ruthenium phosphine complexes was also investigated. Heating a solution of [**1**]Cl and a range of bidentate phosphine (P−P) ligands in methanol solution at reflux afforded a series of complexes [RuCl(κ^2-P-P)(κ^3-tach)]Cl, (P−P = dppm [**3a**]Cl, P−P = dppe [**3b**]Cl, P−P = dppp [**3c**]Cl, P−P = dppb [**3d**]Cl, P−P = dppv [**3e**]Cl, P−P = dppben [**3f**]Cl) (Scheme 4). The cations with general structure [**3**]$^+$ all shared a common series of spectroscopic features. Using [**3a**]Cl as an example, the ^{31}P{^{1}H} NMR spectrum displayed a single resonance for the coordinated dppm ligand at δ_P 10.1, and the ^{1}H NMR spectrum indicated that the tach ligand possessed local C_s symmetry. In contrast to the corresponding reactions between the nitrogen-based ligands, no evidence for

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complexes Reported

metric	[**1**]PF$_6$	[**2a**][PF$_6$]$_2$	[**2b**][PF$_6$]$_2$·MeOH	[**2c**][Cl][PF$_6$]	[**3a**]PF$_6$	[**3b**]PF$_6$	[**3c**]Cl·(H$_2$O)$_{2.15}$·MeOH	[**3d**]Cl·(H$_2$O)$_4$	[**3e**](H$_3$O)$_{0.5}$(Cl)$_{1.5}$H$_2$O	[**3f**]Cl·(CH$_3$OH)$_3$
Ru(1)–N(1)	2.1255(18)	2.136(3)	2.1470(17)	2.1665(13)	2.119(4)	2.135(4)	2.1333(16)	2.139(4)	2.1266(15)	2.124(2)
Ru(1)–N(2)	2.137(2)	2.141(3)	2.1470(17)	2.1396(14)	2.171(4)	2.173(5)	2.1818(16)	2.172(4)	2.1932(15)	2.181(2)
Ru(1)–N(3)	2.135(2)	2.148(3)	2.1333(16)	2.1316(14)	2.162(4)	2.173(5)	2.1846(16)	2.174(5)	2.2003(15)	2.182(2)
Ru(1)–S(1)	2.2581(5)	2.2223(8)	2.2145(8)	2.1885(4)						
Ru(1)–S(2)	2.2524(5)									
Ru(1)–Cl(1)	2.4170(6)				2.4139(12)	2.4431(14)	2.4404(4)	2.4379(12)	2.4415(4)	2.4426(6)
S(1)–O(1)	1.5011(18)	1.500(2)	1.5016(15)	1.5008(12)						
S(2)–O(2)	1.4883(17)									
Ru(1)–N(4)		2.077(3)	2.0881(17)	2.1262(14)						
Ru(1)–N(5)		2.076(2)	2.1008(16)	2.1373(14)						
Ru(1)–P(1)					2.2625(12)	2.230(11)	2.2721(5)	2.2872(13)	2.2661(5)	2.2756(6)
Ru(1)–P(2)					2.2610(12)	2.320(13)	2.2836(5)	2.2860(14)	2.2699(5)	2.2657(6)
N(1)–Ru(1)–N(2)	88.30(8)	87.60(11)	87.79(7)	88.67(5)	87.65(16)	87.64(17)	90.77(6)	86.67(16)	88.84(6)	88.37(8)
N(2)–Ru(1)–N(3)	85.89(8)	88.71(11)	89.26(7)	83.26(6)	87.84(16)	84.58(17)	82.11(7)	82.67(17)	83.50(6)	84.43(8)
N(1)–Ru(1)–N(3)	88.49(8)	85.96(11)	85.79(7)	92.00(5)	88.10(16)	87.61(18)	87.28(6)	87.22(16)	87.18(6)	87.37(8)
S(1)–Ru(1)–Cl(1)	96.04(2)									
N(1)–Ru(1)–Cl(1)	173.36(5)									
N(1)–Ru(1)–S(1)	87.70(6)	175.10(8)	176.39(5)	176.71(4)						
N(2)–Ru(1)–S(1)	171.02(6)	88.28(8)	89.12(5)	94.02(4)						
S(1)–Ru(1)–S(2)	97.49(2)									
S(2)–Ru(1)–Cl(1)	92.37(2)									
N(4)–Ru(1)–N(5)		78.79(10)	79.23(7)	81.59(5)						
N(2)–Ru(1)–N(4)		174.12(10)	175.80(6)	173.67(6)						
N(3)–Ru(1)–N(5)		173.45(10)	175.16(6)	170.62(6)						
N(1)–Ru(1)–N(4)		87.70(10)	88.50(7)	87.66(6)						
N(4)–Ru(1)–S(1)		96.58(7)	94.64(5)	89.83(4)						
P(1)–Ru(1)–P(2)					72.30(4)	82.7(4)	89.481(17)	92.98(5)	83.207(17)	84.00(2)
N(2)–Ru(1)–P(1)					170.48(12)	175.3(2)	173.01(5)	173.32(12)	177.59(5)	178.69(6)
N(3)–Ru(1)–P(2)					171.61(11)	174.0(2)	172.47(5)	174.30(12)	178.34(4)	179.52(6)
N(1)–Ru(1)–Cl(1)					168.19(12)	170.35(13)	169.78(4)	168.19(12)	172.04(4)	169.11(6)
N(2)–Ru(1)–Cl(1)					84.52(12)	85.20(13)	84.98(5)	85.77(11)	84.21(4)	83.49(6)
N(1)–Ru(1)–P(1)					98.29(12)	90.7(3)	94.67(5)	96.17(12)	93.32(4)	92.93(6)
P(1)–Ru(1)–Cl(1)					90.67(4)	96.9(2)	88.939(17)	90.44(4)	93.562(16)	95.21(2)

Table 2. [9]aneS_3 = 1,4,7-trithiacyclononane, Cpˆ = η^5-1-methoxy-2,4-*tert*-butyl-3-neopentylcyclopentadienyl, (L_{OEt} = (η^5-C_5H_5)Co{P(O)(OEt)$_2$}$_3$), Ind = η^5-C_5H_9, Tp^{iPr} = hydro*tris*(3,5-diisopropylpyrazolyl)borate, Tpm = *tris*(pyrazolyl)methane

fac	Ru–S(1)	Ru–S(2)	S(1)–O(1)	S(2)–O(2)	Ru–Cl	ref
			[RuCl(fac)(S-DMSO)$_2$]			
tach	2.2581(5)	2.2524(5)	1.5011(18)	1.4883(17)	2.4170(6)	
Tp	2.288(1)	2.250(1)	1.480(2)	1.482(2)	2.414(1)	26
L_{OEt}	2.186(2)	2.190(2)	1.472(5)	1.476(6)	2.362(2)	27
[9]aneS_3	2.325(1)	2.338(4)	1.485(3)	1.481(3)	2.420(1)	28
Cp*	2.303(3)	2.299(3)	1.485(3)	1.471(3)	2.447(3)	29
	Ru–N(4)	Ru–N(5)	S(1)–O(1)		Ru–S(1)	ref
			[Ru(fac)(bipy)(S-DMSO)]			
tach	2.077(3)	2.076(2)	1.500(2)		2.2223(8)	
[9]aneS_3	2.071(7)	2.100(7)	1.487(8)		2.285(3)	17a
	Ru–P(1)	Ru–P(2)	Ru–Cl		P(1)–Ru–P(2)	
			[RuCl(fac)(dppm)]			
tach	2.2625(12)	2.2610(12)	2.4139(12)		72.30(4)	
Cp	2.2724(5)	2.2833(6)	2.4302(6)		72.07(2)	22
Cp*	2.282(2)	2.294(2)	2.434(2)		71.53(6)	30
Cpˆ	2.3289(16)	2.3459(16)	2.4567(15)		71.32(6)	31
p-cymene	2.316(2)	2.309(2)	2.397(2);		71.29(6)	32
			[RuCl(fac)(dppe)]			
tach	2.230(11)	2.320(13)	2.4431(14)		82.7(4)	
Cp	2.2688(7)	2.2863(7)	2.4466(7)		83.04(3)	22
	2.275(2)	2.282(2)	2.452(2)		83.5(1)	21
Cp*	2.2882(5)	2.2812(5)	2.4532(5)		82.15(2)	30
Cpˆ	2.353(3)	2.360(3)	2.452(2)		82.22(9)	31
$C_{60}Me_5$	2.3657(11)	2.3496(12)	2.4397(11)		82.30(4)	33
Tpm	2.313(3)	2.287(3)	2.397(3)		84.46(11)	34
Tp^{iPr}	2.285(3)	2.279(3)	2.359(4)		85.3(1)	35
Ind	2.2314(4)	2.2970(4)	2.4331(4)		82.171(13)	36
p-cymene	2.329(1)	2.336(1)	2.430(1)		83.03(3)	32
			[RuCl(fac)(dppp)]			
tach	2.2721(5)	2.2836(5)	2.4404(4)		89.481(17)	
Tpm	2.3235(9)	2.3035(9)	2.4056(8)		93.58(3)	37
			[RuCl(fac)(dppb)]			
tach	2.2872(13)	2.2860(14)	2.4379(12)		92.98(5)	
toluene	2.322(2)	2.349(2)	2.399(2)		92.30(7)	38
Cp	2.2810(5)	2.2809(6)	2.4404(4)		93.64(2)	39
Ind	2.2502 (9)	2.2968 (8)	2.4467 (8)		94.88 (3)	40

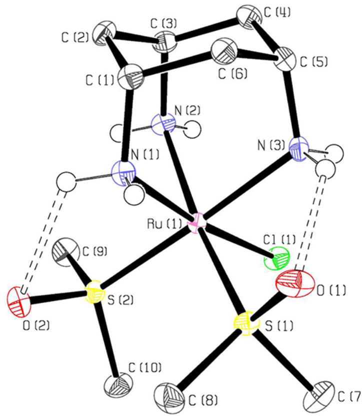
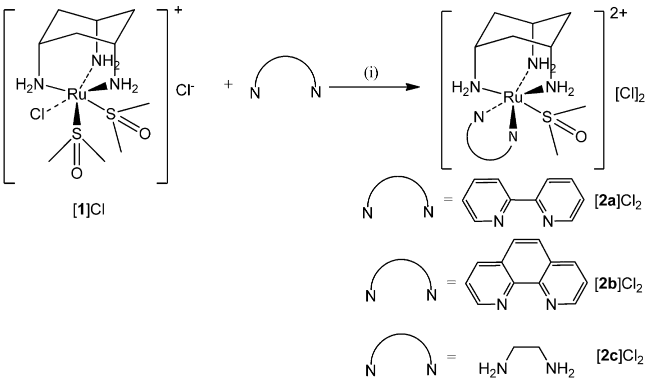


Figure 1. ORTEP diagram of the cation [**1**]$^+$, ellipsoids are shown at the 50% probability level and hydrogen atoms (except for the NH_2-groups) omitted for clarity.

Scheme 3[a]



[a] (i) H_2O, 120 °C, 20 min.

DMSO coordination to the metal was obtained. No resonances were present in the ^1H NMR spectrum for a coordinated DMSO, and in the mass spectrum the only ions observed were due to the chloride-containing complexes (e.g., for [**3a**]$^+$ a peak with the expected isotope pattern at *m/z* 650.1213 corresponding to [RuCl(dppm)(tach)]$^+$ was observed).

All of the complexes [**3**]Cl could be isolated in an analytically pure form without the need for anion metathesis. Crystals

Table 3. Details of the Data Collection and Structure Refinements for All Complexes Reported in This Work

	[**1**]PF_6	[**2a**][PF_6]$_2$	[**2b**][PF_6]$_2$·MeOH	[**2c**][Cl][PF_6]
empirical formula	$C_{10}H_{27}ClF_6N_3O_2PRuS_2$	$C_{18}H_{29}F_{12}N_5OP_2RuS$	$C_{21}H_{33}F_{12}N_5O_2P_2RuS$	$C_{10}H_{29}ClF_6N_5OPRuS$
formula weight	566.96	754.53	810.59	548.93
temperature/K	110	110(2)	110(2)	110(2)
wavelength/Å	0.71073	0.71073	0.71073	0.71073
crystal system	orthorhombic	monoclinic	triclinic	monoclinic
space group	*Aba*2	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a/Å,	14.7124(6)	17.934(3),	9.947(4),	9.5843(8),
b/Å	15.6131(7)	10.6572(16),	10.678(4),	11.4320(10),
c/Å	17.1848(7)	13.783(2)	16.409(6)	18.2955(16)
α/deg	90	90	93.116(7)	90
β/deg	90	90.055(4)	107.140(7)	90.604(2)
γ/deg	90	90	114.478(7)	90
volume/Å^3	3947.5(3)	2634.2(7)	1484.2(10)	2004.5(3)
Z	8	4	2	4
ρ (calculated)/mg/m^{-3}	1.908	1.903	1.814	1.819
absorption coefficient/mm^{-1}	1.288	0.906	0.813	1.164
F(000)	2288	1512	816	1112
crystal size/mm^3	0.21 × 0.16 × 0.15	0.16 × 0.13 × 0.07	0.25 × 0.18 × 0.16	0.40 × 0.19 × 0.08
θ range for data collection/°	2.24 to 28.30	2.22 to 28.32	2.14 to 28.40	2.10 to 28.29
index ranges	$-19 \le h \le 19$	$-23 \le h \le 23$	$-13 \le h \le 13$	$-12 \le h \le 12$
	$-20 \le k \le 20$	$-14 \le k \le 13$	$-14 \le k \le 14$	$-15 \le k \le 15$
	$-22 \le l \le 22$	$-18 \le l \le 18$	$-21 \le l \le 21$	$-24 \le l \le 24$
reflections collected	19637	26643	15239	20281
independent reflections	4902 [R_{int} = 0.0340]	6527 [R_{int} = 0.0546]	7276 [R_{int} = 0.0234]	4979 [R_{int} = 0.0206]
completeness to θ	100% (θ = 28.30°)	99.3% (θ = 28.32°)	97.8% (θ = 28.30°)	99.9% (θ = 28.29°)
max. and min transmission	0.824 and 0.648	0.9393 and 0.8686	0.878 and 0.663	0.911 and 0.771
data/restraints/parameters	4902/22/306	6527/0/388	7276/6/468	4979/0/277
GOF on F^2	1.055	1.024	1.056	1.064
final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0236	R_1 = 0.0407	R_1 = 0.0285	R_1 = 0.0213
	wR_2 = 0.0588	wR_2 = 0.0905	wR_2 = 0.0746	wR_2 = 0.0517
R indices (all data)	R_1 = 0.0239	R_1 = 0.0580	R_1 = 0.0313	R_1 = 0.0234
	wR_2 = 0.0590	wR_2 = 0.0997	wR_2 = 0.0767	wR_2 = 0.0529
largest diff. peak and hole/e Å^{-3}	2.352 and −0.610	0.999 and −0.784	0.832 and −0.677	0.627 and −0.395
absolute structure parameter	−0.01(2)			

Table 3. continued

	[**3a**]PF$_6$	[**3b**]PF$_6$	[**3c**]Cl·(H$_2$O)$_{2.15}$·MeOH	[**3d**]Cl·(H$_2$O)$_4$	[**3e**](H$_3$O)$_{0.5}$(Cl)$_{1.5}$H$_2$O	[**3f**]Cl·(CH$_3$OH)$_3$
empirical formula	$C_{31}H_{37}ClF_6N_3P_3Ru$	$C_{32}H_{39}ClF_6N_3P_3Ru$	$C_{34}H_{47}Cl_2N_3O_{3.15}P_2Ru$	$C_{34}H_{51}Cl_2N_3O_4P_2Ru$	C32H40.5Cl2N3O1.5P2Ru	$C_{39}H_{51}Cl_2N_3O_3P_2Ru$
formula weight	795.07	809.09	782.10	799.69	724.58	843.74
temperature/K	130(2)	110(2)	110.0	110.00(10)	110.00(10)	110.0
wavelength/Å	0.71073	0.7107	0.7107	0.7107	0.7107	0.7107
crystal system	triclinic	trigonal	monoclinic	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P3c1$	$P2_1/n$	$P\bar{1}$	$P21/a$	Cc
a/Å	11.2999(13)	18.9550(7)	9.70362(19)	8.8119(7)	16.9554(3)	18.3263(7)
b/Å	15.1247(17)	18.9550(7)	20.1181(4)	10.6377(9)	9.90919(14)	8.5294(2)
c/Å	20.609(2)	16.9765(6)	17.9253(4)	20.0033(13)	20.2316	26.4162(13)
α/deg	79.083(3)	90	90	75.110(7)	90.00	90
β/deg	89.207(2)	90	94.431(2)	88.833(6)	113.859(3)	109.141(5)
γ/deg	69.075(2)	90	90	78.932(7)	90.00	90
volume/Å^3	3224.9(6)	5282.3(5)	3488.89(13)	1777.6(2)	3108.72(11)	3900.9(3)
Z	4	6	4	2	4	4
ρ (calculated)/mg/m^{-3}	1.638	1.526	1.489	1.494	1.548	1.437
absorption coefficient/mm^{-1}	0.781	0.717	0.733	0.723	0.813	0.662
F(000)	1616	2472	1621	832.0	1494.0	1752
crystal size/mm^3	0.10 × 0.09 × 0.08	0.1754 × 0.099 × 0.0707	0.1919 × 0.132 × 0.1156	0.2867 × 0.1014 × 0.0562	0.2954 × 0.2458 × 0.0541	0.1549 × 0.1457 × 0.0797
θ range for data collection/°	1.01 to 25.06	3.22 to 29.00	2.92 to 32.15	2.79 to 31.76	3.01 to 32.11	2.90 to 30.05
index ranges	$-13 \le h \le 13$	$-21 \le h \le 16$	$-13 \le h \le 12$	$-13 \le h \le 13$	$-25 \le h \le 16$	$-25 \le h \le 25$
	$-18 \le k \le 17$	$-23 \le k \le 25$	$-21 \le k \le 29$	$-15 \le k \le 15$	$-14 \le k \le 13$	$-11 \le k \le 12$
	$-24 \le l \le 24$	$-12 \le l \le 23$	$-12 \le l \le 26$	$-28 \le l \le 29$	$-28 \le l \le 30$	$-34 \le l \le 34$
reflections collected	26296	11946	18989	12956	17028	22702
independent reflections	11364 [R_{int} = 0.0419]	5256 [R_{int} = 0.0334]	10808 [R_{int} = 0.0267]	12956 [R_{int} = 0.0000]	9680 [R(int) = 0.0244]	9763 [R_{int} = 0.0336]
completeness to θ	99.4% (θ = 25.06°)	99.6% (θ = 29.00°)	99.8% (θ = 32.15°)	99.0% (θ = 31.76°)	99.34% (θ = 64.22°)	99.8% (θ = 30.05°)
max. and min transmission	0.939 and 0.745	1.000 and 0.925	0.986 and 0.979	1.000 and 0.100	1.000 and 0.709	0.989 and 0.981
Data/restraints/parameters	11364/54/899	5256/13/511	10808/0/451	12956/0/428	9680/9/445	9763/2/484
GOF on F^2	1.040	1.044	1.034	1.084	1.073	1.035
final R indices [$I > 2\sigma(I)$]	R_1 = 0.0435	R_1 = 0.0417	R_1 = 0.0344	R_1 = 0.0666	R1 = 0.0314,	R_1 = 0.0283
	wR_2 = 0.1024	wR_2 = 0.0987	wR_2 = 0.0761	wR_2 = 0.1943	wR2 = 0.0689	wR_2 = 0.0570
R indices (all data)	R_1 = 0.0684	R_1 = 0.0486	R_1 = 0.0442	R_1 = 0.0734	R1 = 0.0403,	R_1 = 0.0305
	wR_2 = 0.1130	wR_2 = 0.1040	wR_2 = 0.0813	wR_2 = 0.2037	wR2 = 0.0737	wR_2 = 0.0585
largest diff. peak and hole/e Å^{-3}	1.504 and −0.655	0.844 and −0.487	0.582 and −0.913	3.36 and −3.61	0.83 and −0.84	0.410 and −0.402
absolute structure parameter						

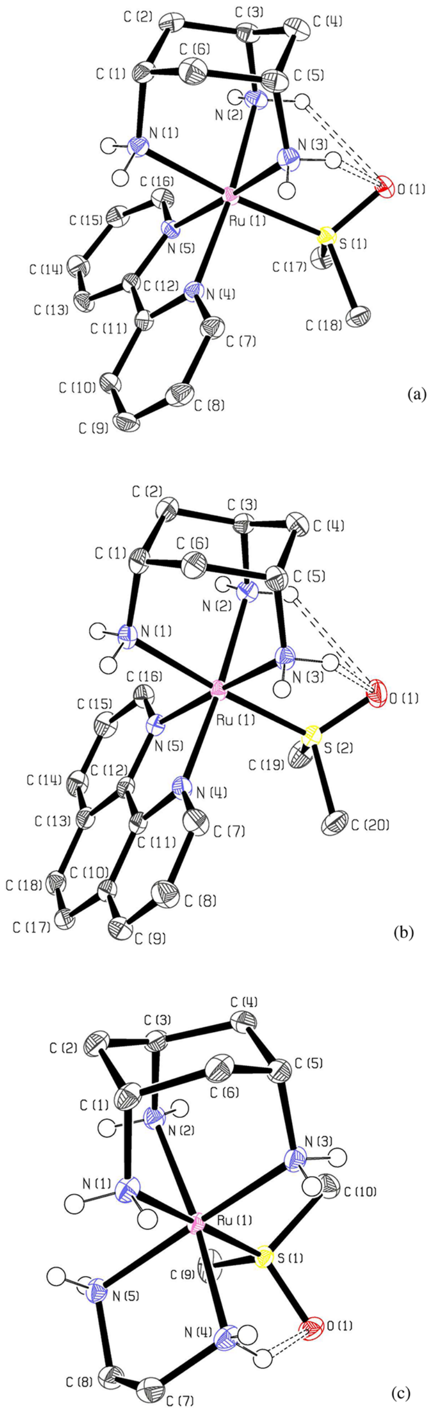


Figure 2. ORTEP diagrams of the dications (a) $[\mathbf{2a}]^{2+}$, (b) $[\mathbf{2b}]^{2+}$, and (c) $[\mathbf{2c}]^{2+}$. Ellipsoids are shown at the 50% probability level and hydrogen atoms (except for the NH_2-groups) omitted for clarity.

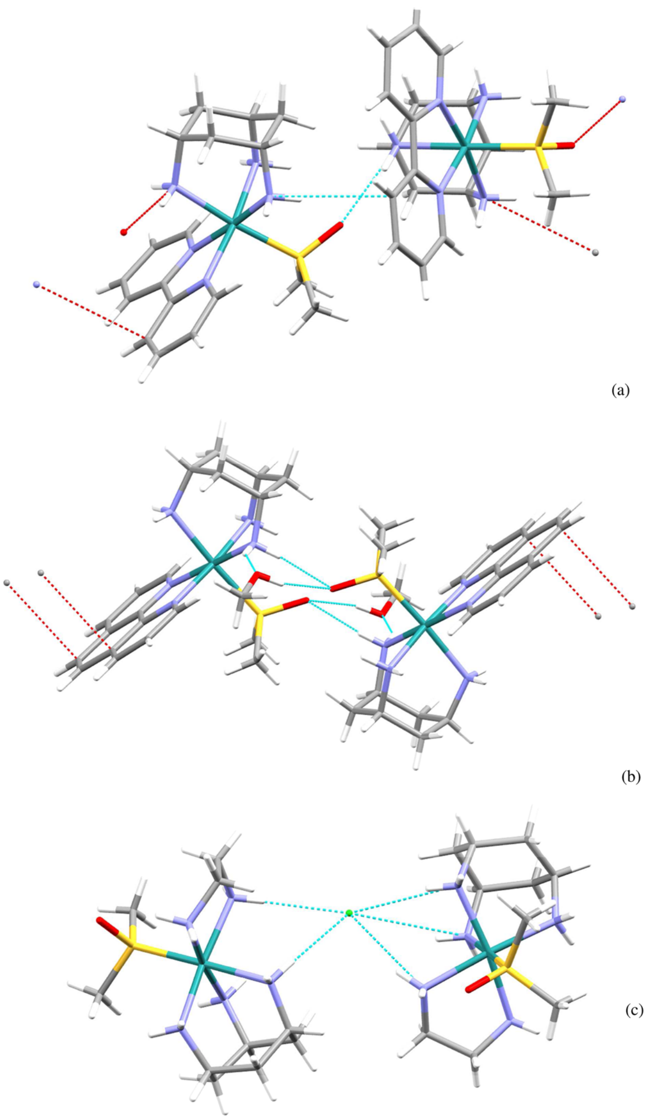
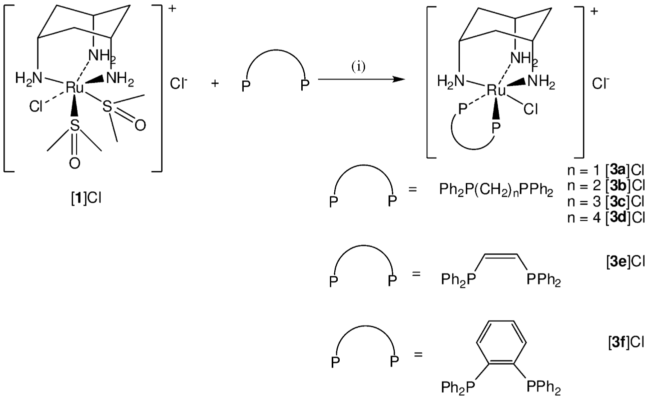


Figure 3. Hydrogen bonding motifs observed in the solid state structures of compounds (a) $[\mathbf{2a}](PF_6)_2$, (b) $[\mathbf{2b}](PF_6)_2{\cdot}MeOH$, (c) $[\mathbf{2c}]Cl(PF_6)$.

Scheme 4[a]



[a](i) MeOH, reflux, 18 h.

suitable for single crystal X-ray diffraction of [**3c**−**f**]Cl could be obtained as the chloride salts, for the dppm and dppe analogue crystals of the corresponding PF_6 salts ([**3a**]PF_6 and [**3b**]PF_6) were employed for the structural determination. The subsequent structural determinations demonstrated that the cationic components of the complexes were essentially isostructural (Figure 4), and in each case the ruthenium was shown to be coordinated to a tach, chelating phosphine and a chloride ligand. With the use of [**3a**]PF_6 as an example, the structure of the complex adopts that of a distorted octahedron at the metal center and the ruthenium tach adamantane moiety is also distorted and tilted in comparison to the octahedron. This is evident from the Ru−N bond lengths of 2.119(4) Å for

Figure 4. ORTEP diagrams of the cations (a) [**3a**]$^+$, (b) [**3b**]$^+$, (c) [**3c**]$^+$, (d) [**3d**]$^+$, (e) [**3e**]$^+$, and (f) [**3f**]$^+$. Ellipsoids are shown at the 50% probability level and hydrogen atoms (except for the NH_2-groups) omitted for clarity.

the amine *trans*- to the chlorido ligand versus 2.171(4) and 2.162(4) Å for those *trans*- to phosphine as a result of the different *trans*-influence of the two ligands. The dppm ligand forms a four-membered ring with the ruthenium center, with a bite angle of 72.30(4)°, significantly smaller than the idealized 90°. The chelating phosphine is also angled away from the N(1) of tach by approximately 20°, which may be the result of N–H···π hydrogen-bonds between the phenyl rings and the amine of the tach group: this is a common feature of all of the cations. Therefore, the phenyl rings adjacent to the chloride ligand are twisted apart, removing the bulky groups from the locality of the metal center.

The structures of [**3a**]PF_6 and [**3b**]PF_6 also show the presence of long-range order. The cations in [**3a**]PF_6 form linear hydrogen-bonded chains; (Figure 5a) which involve a bifurcated hydrogen bond between the chloride ligand on one ruthenium with an NH_2 group on neighboring tach ligand [Cl(1)···N(4) 3.179(5) Å]. The crystals of [**3b**]PF_6 grew in the trigonal space group *P*3*c*1, resulting in a hexagonal morphology. The cations of [**3b**]$^+$ form trigonal and hexagonal motifs around the hexafluorophosphate anions, located on special positions (Figure 5b). A single anion and the dppe ligand are disordered across two sites in the structural solution. A hydrophobic solvent channel is present around one of the anions, but it did not prove to be possible to model this channel; therefore the SQUEEZE algorithm within PLATON was employed.[23] The remaining complexes of general type [**3**]$^+$ do not exhibit strong hydrogen-bonding interactions between the cations within the solid state structure; hydrogen-bonding between the solvent and the cation are the dominant intermolecular interactions.

■ EVALUATION OF THE TACH LIGAND AS A FACIALLY CAPPING GROUP

Selected structural metrics for the complexes prepared in this study are presented in Table 1, in addition, the comparison of

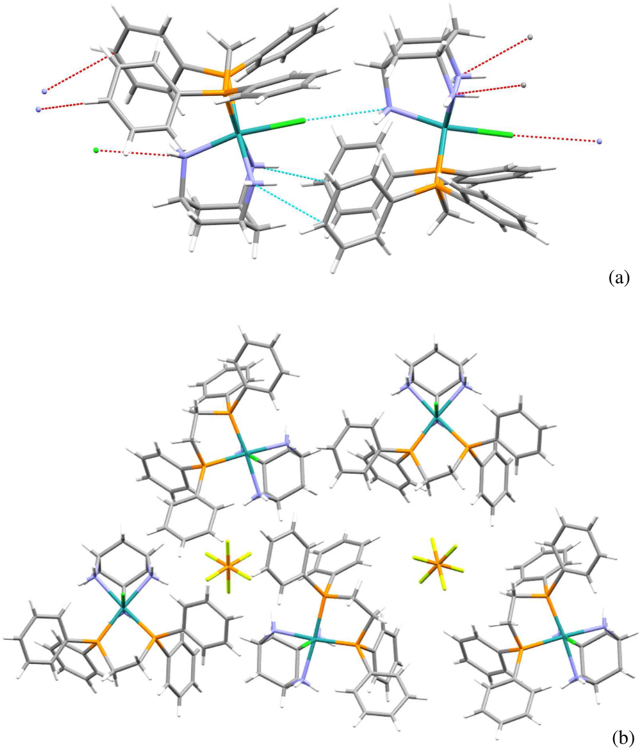


Figure 5. (a) Diagram of the asymmetric unit and the intermolecular hydrogen-bonds within the linear chains of cations in [**3a**]PF_6. (b) Diagram of the trigonal structures in [**3b**]PF_6.

complexes containing the tach ligand and other facially capping groups are in Table 2. In all cases the complexes exhibit a distorted octahedral coordination environment with the tach ligand occupying three coordination sites; however, because of the geometrical constraints of the cyclohexane ring, a nonidealized geometry is obtained. With the use of complex [**1**]PF_6 as an example, the angles subtended by the three nitrogen atoms of the tach ligand are all less than 90° [N(1)–Ru(1)–N(2) 88.30(8) °, N(2)–Ru(1)–N(3) 85.89(8) °, N(1)–Ru(1)–N(3) 88.49(8) °] whereas the angles between the remaining three donor atoms are all considerable greater [S(1)–Ru(1)–Cl(1) 96.04(2) °, S(1)–Ru(1)–S(2) 97.49(2) °, S(2)–Ru(1)–Cl(1) 92.37(2) °]. In addition, all of the angles between the nitrogen atoms of the tach ligand and the chloride and DMSO ligands are notably less than the idealized 180° [N(1)–Ru(1)–Cl(1) 173.36(5) °, N(2)–Ru(1)–S(1) 171.02(6) °, N(3)–Ru(1)–S(2) 176.42(6) °]. This general pattern is repeated in the structures of all of the complexes, although in the cases where bidentate ligands are present, the nature of the bridge linking the donor atoms ensure that angles between these groups are often less than 90°.

A comparison of the bond lengths found within these tach-containing complexes and others containing common facially capping groups appears to demonstrate that tach may be considered to be a hard-type donor ligand, resulting in an electron-rich ruthenium center. For example, in the case of complexes of structure [RuCl(*fac*)(DMSO-*S*)], the Ru–S bond lengths found in complex [**1**]PF_6 are shorter than those found in the cases where the facially coordinating ligand (*fac*) is either Tp, [9]aneS_3, or Cp*, but longer than those found when the hard π-donor $L_{(OEt)}$ is present. In addition, an examination of the sulfur–oxygen bonds reveals that the S(1)–O(1) bond in the structure of [**1**]PF_6 is the longest in this type of complex, although the data must be treated with some caution as the DMSO ligand in [**1**]PF_6 is involved in hydrogen bonding to the tach ligand. The ruthenium–sulfur bond in DMSO complexes is dependent on both σ- and π-components and the length of the S–O bond may be used to probe the nature of the π-interaction.[24] In general, the longer the S–O bond, the greater amount of π-back-donation is occurring into the S–O π^* orbital,[25] thus indicating that the ruthenium center in the tach-containing complex is more electron rich that at least the Tp, [9]aneS_3, or Cp* analogues. The metal chloride bond lengths in this series do not show any significant variation.

It should also be noted that attempts to substitute the DMSO ligand in complexes $[\mathbf{2}]^{2+}$ were unsuccessful, which is consistent with the short metal–sulfur bond lengths as shown by X-ray diffraction and also the unusual position of the S–O stretching frequency in the IR spectrum of the complexes ($[\mathbf{2a}]^{2+}$ 1015 cm^{-1}, $[\mathbf{2b}]^{2+}$ 1016 cm^{-1}, and $[\mathbf{2c}]^{2+}$ 1035 cm^{-1}). The difference in reactivity exhibited by complex [**1**]PF_6 toward diamine and diphosphine ligands is also worthy of note. In the case of the nitrogen-based ligands the dications $[\mathbf{2}]^{2+}$ are formed in which a DMSO ligand remains in the coordination sphere of the metal. In contrast, for the reaction with diphosphine ligands the monocations $[\mathbf{3}]^{+}$ are generated in which the coordination sphere is completed by tach and a chloride ligand. This difference in behavior may be rationalized on the basis of the different π-accepting character of the ligands in question. The diamine ligands are relatively poor π-acceptors; therefore in the electron-rich metal environment created by the tach ligand extensive π-back-donation to the DMSO ligand will occur, thus strengthening the metal–sulfur interaction and disfavoring substitution. Such an argument is supported by the structural arguments presented above. In contrast, diphosphine ligands are considerably better π-acceptors than the diamines, hence favoring an additional π-donor (chloride), as opposed to a π-acceptor (DMSO) in the coordination sphere of the metal although such a preference is clearly apparent, it is exacerbated by the presence of hard nature of the tach ligand.

In conclusion, versatile synthetic routes to a range of complexes containing the facially capping tach ligand have been developed. An analysis of the structural parameters and chemical reactivity indicates that this ligand is a hard donor and that the ruthenium center is extremely electron rich. This factor may also permit the isolation of the ruthenium cations as their chloride salts which exhibit good water solubility.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF with details of X-ray data collection and refinement for complexes reported. Complete experimental details for the synthesis and characterization of all novel compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful to the EPSRC (DTA Studentship for A.J.G.) for funding.

■ REFERENCES

(1) Davies, S. G.; McNally, J. P.; Smallridge, A. J. *Adv. Organomet. Chem.* **1990**, *30*, 1−76.

(2) (a) Bruneau, C.; Dixneuf, P. H. *Acc. Chem. Res.* **1999**, *32*, 311−323. (b) Trost, B. M.; Toste, F. D.; Pinkerton, A. B. *Chem. Rev.* **2001**, *101*, 2067−2096. (c) Trost, B. M.; Frederiksen, M. U.; Rudd, M. T. *Angew. Chem., Int. Ed.* **2005**, *44*, 6630−6666. (d) Bruneau, C.; Dixneuf, P. H. *Angew. Chem., Int. Ed.* **2006**, *45*, 2176−2203. (e) Trost, B. M.; McClory, A. *Chem.—Asian J.* **2008**, *3*, 164−194.

(3) (a) Schauer, P. A.; Low, P. J. *Eur. J. Inorg. Chem.* **2012**, 390−411. (b) Bruce, M. I.; Low, P. J. Transition metal complexes containing all-carbon ligands. In *Advances in Organometallic Chemistry*; West, R., Hill, A. F., Eds.; Academic Press: New York, **2004**; Vol. *50*, pp 179−444; (c) Fox, M. A.; Farmer, J. D.; Roberts, R. L.; Humphrey, M. G.; Low, P. J. *Organometallics* **2009**, *28*, 5266−5269. (d) Fox, M. A.; Roberts, R. L.; Khairul, W. M.; Hartl, F.; Low, P. J. *J. Organomet. Chem.* **2007**, *692*, 3277−3290. (e) Koentjoro, O. F.; Low, P. J.; Rousseau, R.; Nervi, C.; Yufit, D. S.; Howard, J. A. K.; Udachin, K. A. *Organometallics* **2005**, *24*, 1284−1292. (f) Low, P. J. *Dalton Trans.* **2005**, 2821−2824. (g) Low, P. J.; Bruce, M. I. *Adv. Organomet. Chem.* **2001**, *48*, 71−288. (h) Roberts, R. L.; Schwich, T.; Corkery, T. C.; Cifuentes, M. P.; Green, K. A.; Farmer, J. D.; Low, P. J.; Marder, T. B.; Samoc, M.; Humphrey, M. G. *Adv. Mater.* **2009**, *21*, 2318−2322.

(4) (a) Allardyce, C. S.; Dyson, P. J. *Platinum Met. Rev.* **2001**, *45*, 62−69. (b) Allardyce, C. S.; Dorcier, A.; Scolaro, C.; Dyson, P. J. *Appl. Organomet. Chem.* **2005**, *19*, 1−10. (c) Dyson, P. J.; Sava, G. *Dalton Trans.* **2006**, 1929−1933. (d) Kostova, I. *Curr. Med. Chem.* **2006**, *13*, 1085−1107. (e) Dougan, S. J.; Sadler, P. J. *Chimia* **2007**, *61*, 704−715. (f) Fricker, S. P. *Dalton Trans.* **2007**, 4903−4917. (g) Vock, C. A.; Ang, W. H.; Scolaro, C.; Phillips, A. D.; Lagopoulos, L.; Juillerat-Jeanneret, L.; Sava, G.; Scopelliti, R.; Dyson, P. J. *J. Med. Chem.* **2007**, *50*, 2166−2175. (h) Dutta, B.; Scolaro, C.; Scopelliti, R.; Dyson, P. J.; Severin, K. *Organometallics* **2008**, *27*, 1355−1357. (i) Hartinger, C. G.; Dyson, P. J. *Chem. Soc. Rev.* **2009**, *38*, 391−401. (j) Suess-Fink, G. *Dalton Trans.* **2010**, *39*, 1673−1688.

(5) (a) Bruce, M. I.; Windsor, N. J. *Aust. J. Chem.* **1977**, *30*, 1601−1604. (b) Bruce, M. I.; Hameister, C.; Swincer, A. G.; Wallis, R. C.; Ittel, S. D. *Inorg. Synth* **1982**, *21*, 78−84.

(6) Gemel, C.; Huffman, J. C.; Caulton, K. G.; Mauthner, K.; Kirchner, K. *J. Organomet. Chem.* **2000**, *593*−*594*, 342−353.

(7) (a) Tenorio, M. J.; Mereiter, K.; Puerta, M. C.; Valerga, P. *J. Am. Chem. Soc.* **2000**, *122*, 11230−11231. (b) Campion, B. K.; Heyn, R. H.; Tilley, T. D. *J. Chem. Soc., Chem. Commun.* **1988**, 278−280. (c) Jimenez-Tenorio, M.; Puerta, M. C.; Valerga, P. *Eur. J. Inorg. Chem.* **2004**, 17−32.

(8) (a) Bennett, M. A.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* **1974**, 233−241. (b) Lebozec, H.; Touchard, D.; Dixneuf, P. H. *Adv. Organomet. Chem.* **1989**, *29*, 163−247. (c) Bennett, M. A. *Coord. Chem. Rev.* **1997**, *166*, 225−254. (d) Pigge, F. C.; Coniglio, J. J. *Curr. Org. Chem.* **2001**, *5*, 757−784. (e) Adams, J. R.; Bennett, M. A. *Adv. Organomet. Chem.* **2006**, *54*, 293−331. (f) Therrien, B. *Coord. Chem. Rev.* **2009**, *253*, 493−519.

(9) (a) McNair, A. M.; Boyd, D. C.; Mann, K. R. *Organometallics* **1986**, *5*, 303−310. (b) Hill, A. F. *J. Organomet. Chem.* **1990**, *395*, C35−C38. (c) Sun, N. Y.; Simpson, S. J. *J. Organomet. Chem.* **1992**, *434*, 341−349. (d) Jalon, F. A.; Otero, A.; Rodriguez, A. *J. Chem. Soc., Dalton Trans.* **1995**, 1629−1633. (e) Moreno, B.; Saboetienne, S.; Chaudret, B.; Rodriguez, A.; Jalon, F.; Trofimenko, S. *J. Am. Chem. Soc* **1995**, *117*, 7441−7451. (f) Gemel, C.; Trimmel, G.; Slugovc, C.; Kremel, S.; Mereiter, K.; Schmid, R.; Kirchner, K. *Organometallics* **1996**, *15*, 3998−4004. (g) Gemel, C.; Wiede, P.; Mereiter, K.; Sapunov, V. N.; Schmid, R.; Kirchner, K. *J. Chem. Soc., Dalton Trans.* **1996**, 4071−4076. (h) Gemel, C.; Kickelbick, G.; Schmid, R.; Kirchner, K. *J. Chem. Soc., Dalton Trans.* **1997**, 2113−2117. (i) Gemel, C.; Mereiter, K.; Schmid, R.; Kirchner, K. *Organometallics* **1997**, *16*, 2623−2626. (j) Maruyama, Y.; Ikeda, S.; Ozawa, F. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 689−693. (k) Slugovc, C.; Sapunov, V. N.; Wiede, P.; Mereiter, K.; Schmid, R.; Kirchner, K. *J. Chem. Soc., Dalton Trans.* **1997**, 4209−4216. (l) Tenorio, M. J.; Tenorio, M. A. J.; Puerta, M. C.; Valerga, P. *Inorg. Chim. Acta* **1997**, *259*, 77−84. (m) Trimmel, G.; Slugovc, C.; Wiede, P.; Mereiter, K.; Sapunov, V. N.; Schmid, R.; Kirchner, K. *Inorg. Chem.* **1997**, *36*, 1076−1083. (n) Slugovc, C.; Mauthner, K.; Kacetl, M.; Mereiter, K.; Schmid, R.; Kirchner, K. *Chem.—Eur. J.* **1998**, *4*, 2043−2050. (o) Buriez, B.; Burns, I. D.; Hill, A. F.; White, A. J. P.; Williams, D. J.; Wilton-Ely, J. *Organometallics* **1999**, *18*, 1504−1516. (p) Slugovc, C.; Mereiter, K.; Schmid, R.; Kirchner, K. *Eur. J. Inorg. Chem.* **1999**, 1141−1149.

(10) (a) Yang, S. M.; Cheng, W. C.; Cheung, K. K.; Che, C. M.; Peng, S. M. *J. Chem. Soc., Dalton Trans.* **1995**, 227−230. (b) Yang, S. M.; Cheng, W. C.; Peng, S. M.; Cheung, K. K.; Che, C. M. *J. Chem. Soc., Dalton Trans.* **1995**, 2955−2959. (c) Yang, S. M.; Chan, M. C. W.; Cheung, K. K.; Che, C. M.; Peng, S. M. *Organometallics* **1997**, *16*, 2819−2826.

(11) (a) Day, V. W.; Eberspacher, T. A.; Klemperer, W. G.; Planalp, R. P.; Schiller, P. W.; Yagasaki, A.; Zhong, B. *Inorg. Chem.* **1993**, *32*, 1629−1637. (b) Ikeda, Y.; Yamaguchi, T.; Kanao, K.; Kimura, K.; Kamimura, S.; Mutoh, Y.; Tanabe, Y.; Ishii, Y. *J. Am. Chem. Soc.* **2008**, *130*, 16856−16857.

(12) (a) Goodfellow, B. J.; Felix, V.; Pacheco, S. M. D.; deJesus, J. P.; Drew, M. G. B. *Polyhedron* **1997**, *16*, 393−401. (b) Madureira, J.; Santos, T. M.; Goodfellow, B. J.; Lucena, M.; de Jesus, J. L. P.; Santana-Marques, M. G.; Drew, M. G. B.; Felix, V. *J. Chem. Soc., Dalton Trans.* **2000**, 4422−4431. (c) Santana-Marques, M. G. O.; Amado, F. M. L.; Correia, A. J. F.; Lucena, M.; Madureira, J.; Goodfellow, B. J.; Felix, V.; Santos, T. M. *J. Mass Spectrom.* **2001**, *36*, 529−537. (d) Sala, X.; Poater, A.; Romero, I.; Rodriguez, M.; Llobet, A.; Solans, X.; Parella, T.; Santos, T. M. *Eur. J. Inorg. Chem.* **2004**, 612−618. (e) Sala, X.; Romero, I.; Rodriguez, M.; Llobet, A.; Gonzalez, G.; Martinez, M.; Benet-Buchholz, J. *Inorg. Chem.* **2004**, *43*, 5403−5409. (f) Iengo, E.; Zangrando, E.; Baiutti, E.; Munini, F.; Alessio, E. *Eur. J. Inorg. Chem.* **2005**, 1019−1031. (g) Marques, J.; Anjo, L.; Marques, M. P. M.; Santos, T. M.; Paz, F. A. A.; Braga, S. S. *J. Organomet. Chem.* **2008**, *693*, 3021−3028. (h) Rilak, A.; Bratsos, I.; Zangrando, E.; Kljun, J.; Turel, I.; Bugarcic, Z. D.; Alessio, E. *Dalton Trans.* **2012**, *41*, 11608−11618.

(13) (a) Arockiam, P. B.; Bruneau, C.; Dixneuf, P. H. *Chem. Rev.* **2012**, *112*, 5879−5918. (b) Ackermann, L. *Acc. Chem. Res.* **2013**, DOI: 10.1021/ar3002798. (c) Johnson, D. G.; Lynam, J. M.; Mistry, N. S.; Slattery, J. M.; Thatcher, R. J.; Whitwood, A. C. *J. Am. Chem. Soc.* **2013**, *135*, 2222−2234.

(14) (a) Allardyce, C. S.; Dyson, P. J.; Ellis, D. J.; Heath, S. L. *Chem. Commun.* **2001**, 1396−1397. (b) Scolaro, C.; Bergamo, A.; Brescacin, L.; Delfino, R.; Cocchietto, M.; Laurenczy, G.; Geldbach, T. J.; Sava, G.; Dyson, P. J. *J. Med. Chem.* **2005**, *48*, 4161−4171. (c) Bergamo, A.; Masi, A.; Dyson, P. J.; Sava, G. *Int. J. Oncol.* **2008**, *33*, 1281−1289. (d) Casini, A.; Gabbiani, C.; Sorrentino, F.; Rigobello, M. P.; Bindoli, A.; Geldbach, T. J.; Marrone, A.; Re, N.; Hartinger, C. G.; Dyson, P. J.; Messori, L. *J. Med. Chem.* **2008**, *51*, 6773−6781. (e) Dorcier, A.; Hartinger, C. G.; Scopelliti, R.; Fish, R. H.; Keppler, B. K.; Dyson, P. J. *J. Inorg. Biochem.* **2008**, *102*, 1066−1076. (f) Renfrew, A. K.; Phillips, A. D.; Egger, A. E.; Hartinger, C. G.; Bosquain, S. S.; Nazarov, A. A.; Keppler, B. K.; Gonsalvi, L.; Peruzzini, M.; Dyson, P. J. *Organometallics* **2009**, *28*, 1165−1172. (g) Phillips, A. D.; Zava, O.; Scopelitti, R.; Nazarov, A. A.; Dyson, P. J. *Organometallics* **2010**, *29*, 417−427. (h) Nowak-Sliwinska, P.; van Beijnum, J. R.; Casini, A.; Nazarov, A. A.; Wagnieres, G.; van den Bergh, H.; Dyson, P. J.; Griffioen, A. W. *J. Med. Chem.* **2011**, *54*, 3895−3902. (i) Renfrew, A. K.; Juillerat-Jeanneret, L.; Dyson, P. J. *J. Organomet. Chem.* **2011**, *696*, 772−779. (j) Tan, Y. Q.; Dyson, P. J.; Ang, W. H. *Organometallics* **2011**, *30*, 5965−5971. (k) Wu, B.; Ong, M. S.; Groessl, M.; Adhireksan, Z.; Hartinger, C. G.; Dyson, P. J.; Davey, C. A. *Chem.—Eur. J.* **2011**, *17*, 3562−3566. (l) Nazarov, A. A.; Risse, J.; Ang, W. H.; Schmitt, F.; Zava, O.; Ruggi, A.; Groessl, M.; Scopelitti, R.; Juillerat-Jeanneret, L.; Hartinger, C. G.; Dyson, P. J. *Inorg. Chem.* **2012**, *51*, 3633−3639.

(15) (a) Morris, R. E.; Aird, R. E.; del Socorro Murdoch, P.; Chen, H.; Cummings, J.; Hughes, N. D.; Parsons, S.; Parkin, A.; Boyd, G.; Jodrell, D. I.; Sadler, P. J. *J. Med. Chem.* **2001**, *44*, 3616−3621. (b) Bugarcic, T.; Habtemariam, A.; Stepankova, J.; Heringova, P.; Kasparkova, J.; Deeth, R. J.; Johnstone, R. D. L.; Prescimone, A.;

Parkin, A.; Parsons, S.; Brabec, V.; Sadler, P. J. *Inorg. Chem.* **2008**, *47*, 11470−11486.

(16) (a) Guichard, S. M.; Else, R.; Reid, E.; Zeitlin, B.; Aird, R.; Muir, M.; Dodds, M.; Fiebig, H.; Sadler, P. J.; Jodrell, D. I. *Biochem. Pharmacol.* **2006**, *71*, 408−415. (b) Habtemariam, A.; Melchart, M.; Fernández, R.; Parsons, S.; Oswald, I. D. H.; Parkin, A.; Fabbiani, F. P. A.; Davidson, J. E.; Dawson, A.; Aird, R. E.; Jodrell, D. I.; Sadler, P. J. *J. Med. Chem.* **2006**, *49*, 6858−6868. (c) Wang, F.; Habtemariam, A.; van der Geer, E. P. L.; Fernández, R.; Melchart, M.; Deeth, R. J.; Aird, R.; Guichard, S.; Fabbiani, F. P. A.; Lozano-Casal, P.; Oswald, I. D. H.; Jodrell, D. I.; Parsons, S.; Sadler, P. J. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 18269−18274. (d) Camm, K. D.; El-Sokkary, A.; Gott, A. L.; Stockley, P. G.; Belyaeva, T.; McGowan, P. C. *Dalton Trans.* **2009**, 10914−10925. (e) Bugarcic, T.; Nováková, O.; Halámiková, A.; Zerzánková, L.; Vrána, O. i.; Kašpárková, J.; Habtemariam, A.; Parsons, S.; Sadler, P. J.; Brabec, V. *J. Med. Chem.* **2008**, *51*, 5310−5319. (f) Bugarcic, T.; Habtemariam, A.; Deeth, R. J.; Fabbiani, F. P. A.; Parsons, S.; Sadler, P. J. *Inorg. Chem.* **2009**, *48*, 9444−9453. (g) Peacock, A. F. A.; Habtemariam, A.; Fernández, R.; Walland, V.; Fabbiani, F. P. A.; Parsons, S.; Aird, R. E.; Jodrell, D. I.; Sadler, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 1739−1748. (h) Caruso, F.; Rossi, M.; Benson, A.; Opazo, C.; Freedman, D.; Monti, E.; Gariboldi, M. B.; Shaulky, J.; Marchetti, F.; Pettinari, R.; Pettinari, C. *J. Med. Chem.* **2011**, *55*, 1072−1081.

(17) (a) Serli, B.; Zangrando, E.; Gianferrara, T.; Scolaro, C.; Dyson, P. J.; Bergamo, A.; Alessio, E. *Eur. J. Inorg. Chem.* **2005**, *2005*, 3423−3434. (b) Bratsos, I.; Jedner, S.; Bergamo, A.; Sava, G.; Gianferrara, T.; Zangrando, E.; Alessio, E. *J. Inorg. Biochem.* **2008**, *102*, 1120−1133. (c) Gianferrara, T.; Bergamo, A.; Bratsos, I.; Milani, B.; Spagnul, C.; Sava, G.; Alessio, E. *J. Med. Chem.* **2010**, *53*, 4678−4690.

(18) Bratsos, I.; Mitri, E.; Ravalico, F.; Zangrando, E.; Gianferrara, T.; Bergamo, A.; Alessio, E. *Dalton Trans.* **2012**, *41*, 7358−7371.

(19) Chen, H.; Parkinson, J. A.; Parsons, S.; Coxall, R. A.; Gould, R. O.; Sadler, P. J. *J. Am. Chem. Soc.* **2002**, *124*, 3064−3082.

(20) (a) Bowen, T.; Planalp, R. P.; Brechbiel, M. W. *Bioorg. Med. Chem. Lett.* **1996**, *6*, 807−810. (b) Brechbiel, M. W.; Tsoupas, N. M.; Ye, N.; Planalp, R. P.; Bauer, C. B.; Rogers, R. D. *Chem. Abstr.* **1996**, *211*, 236-ORGN. (c) Park, G.; Lu, F. H.; Ye, N.; Brechbiel, M. W.; Torti, S. V.; Torti, F. M.; Planalp, R. P. *J. Biol. Inorg. Chem.* **1998**, *3*, 449−457. (d) Park, G.; Dadachova, E.; Przyborowska, A.; Lai, S. J.; Ma, D. S.; Broker, G.; Rogers, R. D.; Planalp, R. P.; Brechbiel, M. W. *Polyhedron* **2001**, *20*, 3155−3163. (e) Samuni, A. M.; Krishna, M. C.; DeGraff, W.; Russo, A.; Planalp, R. P.; Brechbiel, M. W.; Mitchell, J. B. *BBA-Gen. Subjects* **2002**, *1571*, 211−218. (f) Ye, N.; Park, G.; Przyborowska, A. M.; Sloan, P. E.; Clifford, T.; Bauer, C. B.; Broker, G. A.; Rogers, R. D.; Ma, R.; Torti, S. V.; Brechbiel, M. W.; Planalp, R. P. *Dalton Trans.* **2004**, 1304−1311. (g) Zhao, R.; Planalp, R. P.; Ma, R.; Greene, B. T.; Jones, B. T.; Brechbiel, M. W.; Torti, F. M.; Torti, S. V. *Biochem. Pharmacol.* **2004**, *67*, 1677−1688. (h) Childers, M. L.; Su, F.; Przyborowska, A. M.; Bishwokarma, B.; Park, G.; Brechbiel, M. W.; Torti, S. V.; Torti, F. M.; Broker, G.; Alexander, J. S.; Rogers, R. D.; Ruhlandt-Senge, K.; Planalp, R. P. *Eur. J. Inorg. Chem.* **2005**, 3971−3982. (i) Greener, B.; Cronin, L.; Wilson, G. D.; Walton, P. H. *J. Chem. Soc., Dalton Trans.* **1996**, 401−403. (j) Greener, B.; Moore, M. H.; Walton, P. H. *Chem. Commun.* **1996**, 27−28. (k) Cronin, L.; Foxon, S. P.; Lusby, P. J.; Walton, P. H. *J. Biol. Inorg. Chem.* **2001**, *6*, 367−377. (l) Cronin, L.; Walton, P. H. *Chem. Commun.* **2003**, 1572−1573.

(21) Suravajjala, S.; Porter, L. C. *Acta. Crystallogr., Sect. C* **1993**, *49*, 1456−1458.

(22) Pearson, W. H.; Shade, J. E.; Brown, J. E.; Bitterwolf, T. E. *Acta. Crystallogr., Sect. C* **1996**, *52*, 1106−1110.

(23) (a) Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7−13. (b) Spek, A. L. *PLATON, A Multipurpose Crystallographic Tool*; Utrecht University: Utrecht, The Netherlands, 2005.

(24) (a) Calligaris, M.; Carugo, O. *Coord. Chem. Rev.* **1996**, *153*, 83−154. (b) Mario, C. *Coord. Chem. Rev.* **2004**, *248*, 351−375.

(25) Stener, M.; Calligaris, M. *J. Mol. Struct.: THEOCHEM* **2000**, *497*, 91−104.

(26) Rüba, E.; Gemel, C.; Slugovc, C.; Mereiter, K.; Schmid, R.; Kirchner, K. *Organometallics* **1999**, *18*, 2275−2280.

(27) Leung, W.-H.; Chan, E. Y. Y.; Williams, I. D.; Wong, W.-T. *Organometallics* **1997**, *16*, 3234−3240.

(28) Iengo, E.; Zangrando, E.; Baiutti, E.; Munini, F.; Alessio, E. *Eur. J. Inorg. Chem.* **2005**, *2005*, 1019−1031.

(29) Wang, M. H.; Englert, U.; Kölle, U. *J. Organomet. Chem.* **1993**, *453*, 127−131.

(30) Bruce, M. I.; Ellis, B. G.; Low, P. J.; Skelton, B. W.; White, A. H. *Organometallics* **2003**, *22*, 3184−3198.

(31) Dutta, B.; Solari, E.; Gauthier, S.; Scopelliti, R.; Severin, K. *Organometallics* **2007**, *26*, 4791−4799.

(32) Daguenet, C.; Scopelliti, R.; Dyson, P. J. *Organometallics* **2004**, *23*, 4849−4857.

(33) Matsuo, Y.; Mitani, Y.; Zhong, Y.-W.; Nakamura, E. *Organometallics* **2006**, *25*, 2826−2832.

(34) Wilson, D. C.; Nelson, J. H. *J. Organomet. Chem.* **2003**, *682*, 272−289.

(35) Takahashi, Y.; Akita, M.; Hikichi, S.; Moro-oka, Y. *Inorg. Chem.* **1998**, *37*, 3186−3194.

(36) Singh, K. S.; Thöne, C.; Kollipara, M. R. *J. Organomet. Chem.* **2005**, *690*, 4222−4231.

(37) Walker, J. M.; McEwan, A.; Pycko, R.; Tassotto, M. L.; Gottardo, C.; Th'ng, J.; Wang, R.; Spivak, G. J. *Eur. J. Inorg. Chem.* **2009**, 4629−4633.

(38) Thorburn, I. S.; Rettig, S. J.; James, B. R. *J. Organomet. Chem.* **1985**, *296*, 103−114.

(39) van der Drift, R. C.; Gagliardo, M.; Kooijman, H.; Spek, A. L.; Bouwman, E.; Drent, E. *J. Organomet. Chem.* **2005**, *690*, 1044−1055.

(40) Sung, H.-L.; Her, T.-M.; Su, W.-H.; Cheng, C.-P. *Acta Crystallogr., Sect. E* **2011**, *67*, m641.