DOI: 10.1002/ejic.200700025

A Linear Ru-Tl-Ru Complex Obtained from Halide Abstraction: An Example of Metal-Dative Bonding

Ian Bytheway,[a] Christopher S. Griffith,[a][‡] George A. Koutsantonis,*[a] Brian W. Skelton,[a] and Allan H. White[a]

Keywords: Ruthenium / Thallium / AIM calculations / Metal–metal bond

The simple abstraction of chloride ion from [RuCl(CO)$_2$(η-C$_5$H$_5$)] using [TlBF$_4$] proved problematic, unexpectedly giving a new complex containing linear Ru–Tl–Ru. The complex, [{Ru(CO)$_2$(η-C$_5$H$_5$)}$_2$(μ-Tl)(F–BF$_2$–F)]$_\infty$, was polymeric, as determined by a single-crystal X-ray diffraction experiment, in which the thallium centres are bridged by the anions. In an effort to compare the nature of the Tl–Ru bonds, an additional complex was prepared by the reaction of Tl^{3+} ions with [Ru(CO)$_2$(η-C$_5$H$_5$)]$^-$. The resulting neutral complex, [{Ru(CO)$_2$(η-C$_5$H$_5$)}$_3$(μ-Tl)], was also structurally characterised. Quantum chemical calculations of [{Ru(CO)$_2$(η-C$_5$H$_5$)}$_2$(μ-Tl)][BF$_4$] suggest that the Tl–Ru bond has ionic character with integrated atomic charges showing that the metal–metal bonding is best represented as Ru^0–Tl$^{\mathrm{I}}$–Ru^0.
(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2007)

Introduction

Interactions between closed-shell metals and their ions has spawned the field of “metallophilicity”[1–4] which is attracting increasing interest with respect to the photophysical properties of the resulting complexes.[5–8] Additionally there is an interest in the coordination chemistry of low-valent group 13, particularly those transition-metal complexes containing “naked” group 13 atoms as bridging ligands,[9] the thesis being that these atoms should display very strong π-acceptor properties.

In recent work, we have been pursuing the chemistry of the Ru(CO)$_2$(η-C$_5$H$_5$) fragment in various guises[10–19] and have observed that protonation of [{Ru(CO)$_2$(η-C$_5$H$_5$)}$_2$(μ-C≡C)] gave the unexpected trinuclear complex, [{Ru(CO)$_2$(η-C$_5$H$_5$)}$_3$(μ-C≡C)]$^+$.[16] This reaction was irreproducible, but the nature of the product suggested that a more rational and dependable route to its synthesis was the addition of the metal electrophile [Ru(CO)$_2$(η-C$_5$H$_5$)(solvent)]$^+$ to [{Ru(CO)$_2$(η-C$_5$H$_5$)}$_2$(μ-C≡C)]. The unusual chemistry encountered in the attempted syntheses of such *solvento* cations is described below.

Results and Discussion

The synthesis of [Ru(thf)(CO)$_2$(η-C$_5$H$_5$)](BF$_4$) (**1**) by chloride abstraction from the electron-poor complex, [Ru(CO)$_2$(η-C$_5$H$_5$)Cl] (**2**), using [AgBF$_4$] was attempted but the reaction, surprisingly, proved to be problematic. The precipitation of a grey/white material, presumably [AgCl]$_n$, was observed at reflux in thf and the reaction monitored by infrared spectroscopy for 12 h, beyond which the infrared spectrum of the reaction mixture changed minimally. Two new ν(CO) absorptions at 2019 and 2073 cm^{-1} were observed along with those attributable to residual **2**. Recrystallisation of the reaction mixture gave material which appeared to correspond to **1**, contaminated (ca. 5%) with **2**. The analogous abstraction of the halide ions from [Fe(CO)$_2$(η-C$_5$R$_5$)X] (R = H, Me; X = Cl, I) complexes by silver ion in donor solvents is well known, giving the corresponding *solvento* cation,[20–22] although the preparation of complex **1**, to the best of our knowledge, is unreported. Our attempts to use this material in further reactions proved unsuccessful.

The alternative halide-abstraction reagent, [TlBF$_4$], was employed in the attempted removal of the chloride ion from **2**, but instead of the expected *solvento* cation the reaction gave a moderate yield of the 1D polymer, [{Ru(CO)$_2$(η-C$_5$H$_5$)}$_2$(μ-Tl)(F–BF$_2$–F)]$_\infty$ (**3**), the connectivity of which was determined by a single-crystal X-ray structural determination.

The FAB mass spectrum of complex **3** consisted of a base peak at *m/z* 651 corresponding to [M]$^+$. The ^{1}H NMR spectrum had the expected singlet resonance at δ = 5.54 ppm assigned to Ru(η-C$_5$H$_5$), and is comparable to the resonance reported for the complex [Ru(CO)$_2$(η-C$_5$H$_5$)(MeCN)][PF$_6$].[23] The ^{19}F NMR spectrum contains a single, broad resonance at δ = 151.72 ppm, which is inconsistent with the solid-state structure where two fluorine environments are observed suggesting that the polymeric

---

[a] Chemistry, M313, School of Biomedical, Biomolecular and Chemical Sciences, University of Western Australia,
35 Stirling Highway, Crawley, Perth, WA 6009, Australia
Fax: +61-8-6488-7247
E-mail: gak@chem.uwa.edu.au
[‡] Present address: Institute for Materials and Engineering Sciences, Australian Nuclear Science and Technology Organisation, New Illawarra Rd, Lucas Heights NSW 2234, Australia

structure arises from cation–anion contacts imposed to some extent by close packing contraints. The fluxional nature of the complex in solution is highlighted by the infrared spectrum where the three absorptions at 2024, 1999 and 1971 cm^{-1} do not imply an exclusive, relative synclinal orientation of the two cyclopentadienyl ligands as defined by the solid-state structure. In spite of the apparent stability of **3** in the solid state, inconsistent microanalytical results were obtained.

Given the dearth of complexes with Ru–Tl complexes in the literature we decided to add to the examples extant with the reaction of $[Ru(CO)_2(\eta\text{-}C_5H_5)]^-$[24] and $TlCl_3{\cdot}4H_2O$ which gave $[\{Ru(CO)_2(\eta\text{-}C_5H_5)\}_3(\mu_3\text{-}Tl)]$ (**4**) in moderate yield. The infrared spectrum of **4** contains three strong υ(CO) absorptions at 1998, 1972 and 1929 cm^{-1}, reminiscent of the infrared spectrum of $[\{Ru(CO)_2(\eta\text{-}C_5H_5)\}_3(\mu_3\text{-}In)]$.[25] The FAB mass spectrum does not contain a molecular ion but resembles that for complex **3** with an ion assigned to $[\{Ru(CO)_2(\eta\text{-}C_5H_5)\}_2(Tl)]^+$ at *m/z* 651. The ^1H NMR spectrum contains a doublet centred at $\delta = 4.69$ ppm attributed to coupling of the ^{205}Tl nuclei to $Ru(\eta\text{-}C_5H_5)$ ($^3J_{TlH} = 7.9$ Hz).

The complexes $[\{M(CO)_x(\eta\text{-}C_5H_5)\}_3(\mu_3\text{-}Tl)]$ (M = Cr, x = 3, **5**;[26] M = Mo, x = 3, **6**;[26,27] M = W, x = 3, **7**;[26] M = Fe, x = 2, **8**.[28]) are examples of complexes analogous to **4**, although the oxidation state of the thallium in these examples is formally Tl^{III}. Complex **6** has also been prepared from the reaction of $Tl(C_5H_5)$ and $Mo(CO)_6$.[27]

A similar $^2J_{TlH}$ coupling was not observed for complexes **3**, **6**[27] or the complexes $[TlR_2\{M(CO)_2(\eta\text{-}C_5H_5)\}]$ (R = Me, M = Mo; R = Me, M = W; R = Et, M = Mo).[29,30] However, Whitmire and co-workers[28] observed a $^3J_{TlH}$ coupling constant of 26 Hz for **8** and, in accord with these workers, the pair of doublets centered at $\delta = 85.1$ and 202.7 ppm in the ^{13}C NMR spectrum of **4** is assigned to the coupling of the ^{205}Tl nuclei to $Ru(\eta\text{-}C_5H_5)$ ($^2J_{TlC} = 7.8$ Hz) and Ru–CO ($^2J_{TlC} = 279.3$ Hz). These assignments imply a single $\{Ru(CO)_2(\eta\text{-}C_5H_5)\}$ environment in solution which is inconsistent with the solid-state structures and suggests that the $(\eta\text{-}C_5H_5)$ environments are exchanging on the NMR time-scale.

The most relevant literature precedent for **3** is the anion produced in the reaction between $[RuBr(CO)_3(\eta^3\text{-}C_3H_5)]$ and Tl(*closo*-1,2-Me_2-3,1,2-$TlC_2B_9H_9$), viz. $Tl[\{Ru(CO)_2(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)\}_2(\mu\text{-}Tl)]$, which was isolated as the $[NEt_4]^+$ salt, **9**, after metathesis, along with a small amount of the neutral tricarbonyl, $[Ru(CO)_3(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)]$.[31] Most notable in the difference between the compound reported here, **3**, and complex **9** is that the former contains the bridging Tl in a cation while the latter is more typically an anion. The bonding can be described as purely ionic, involving two anionic Ru^{II} centres and the Tl^+ cation, as has been postulated for a number of transition-metal salts containing Tl^+.[31] However, in the light of what the authors considered as relatively short Ru–Tl bonds, it was suggested that a significant covalent interaction might be imparting stability, leading to short Ru–Tl distances in complex **9**, through filled 4d and empty 5p orbitals of suitable symmetry on Ru and the filled 6s and empty 6p orbitals on the thallium atom, based on assertions suggested for the bonding in $[Ir_2(\mu\text{-}Tl)\{\mu\text{-}(PPh_2CH_2)_2AsPh\}_2Cl(CO)_2]^+$.[32] We have explored the bonding in **3** in more detail using ab initio calculations and these will be discussed below.

Solid State Structures of $[\{Ru(CO)_2(\eta\text{-}C_5H_5)\}_2(\mu\text{-}Tl)(F\text{–}BF_2\text{–}F)]$ (3) and $[\{Ru(CO)_2(\eta\text{-}C_5H_5)\}_3(\mu_3\text{-}Tl)]$ (4)

The results of the single-crystal structural determinations of complexes **3** and **4** are presented in Figure 1 and Figure 2 with interatomic parameters collected in Table 1 and details of the determinations in Table 5. Preliminary examination of the Tl–Ru bond lengths present in **3**, suggested they appeared to be very short when compared to the sum of the metallic radii of the two metals (3.03 Å).[33] In the complexes, $[\{Mn(CO)_2(\eta\text{-}C_5H_4R)\}_2(\mu\text{-}E)]$ (E = Ge, R = CH_3; E = Pb, R = H), this comparison of the bond lengths has been used as the prime indicator of multiple bond character between the main and transition-metal centres,[34–37] the most relevant example of this type of complex to **3** being $[\{Cr(CO)_5\}_2(\mu\text{-}Tl)]^-$.[38] Surprisingly, there exist only two crystallographically characterised complexes containing a Tl–Ru bond, the high nuclearity ruthenium carbido clus-

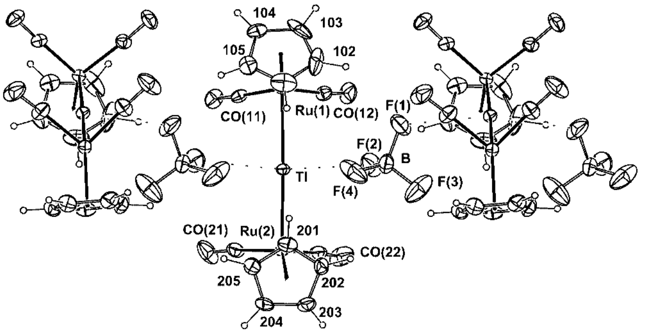

Figure 1. A section of the polymeric strand of **3**.

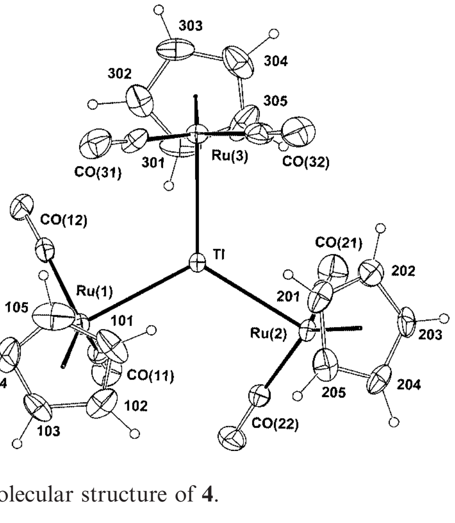

Figure 2. Molecular structure of **4**.

ter,[39] $[\{Ru_6(C)(CO)_{16}\}_2(\mu\text{-}Tl)]^-$, with Tl–Ru bond lengths between 2.775(3)–2.875(2) Å and anionic $[NEt_4][\{Ru(CO)_2(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)\}_2(\mu\text{-}Tl)]$ (**9**),[31] Tl–Ru 2.5994(4) Å.

Table 1. Selected interatomic distances [Å] and angles [°] in compounds **3** ands **4**.[a]

Distances	3	4
Ru(1)–Tl	2.6298(7)	2.7327(8)
Ru(2)–Tl	2.6260(7)	2.7198(8)
Ru(3)–Tl	–	2.7089(8)
Ru(1)–C(11),C(12)	1.870(9), 1.88(1)	1.84(1), 1.90(1)
Ru(2)–C(21),C(22)	1.89(1), 1.86(1)	1.86(1), 1.856(9)
Ru(3)–C(31),C(32)	–	1.86(1), 1.84(1)
Ru(1)–cp(100)	1.88_8	
Ru(2)–cp(200)	1.89_9	
Ru(3)–cp(300)		
C(n1)–O(*n*1)	1.12(1), 1.12(2)	1.16(1), 1.12(1)
C(n2)–O(*n*2)	1.12(2), 1.18(2)	1.16(1), 1.15(1)
C(n3)–O(*n*3)		1.15(2), 1.16(1)
Angles		
Ru(1)–Tl–Ru(2)	176.98(3)	120.04(2)
Ru(1)–Tl–Ru(3)	–	117.39(3)
Ru(2)–Tl–Ru(3)	–	122.57(3)
C(*n*1)–Ru(*n*)–C(*n*2)	93.6(5), 91.2(6)	88.8(4), 90.9(4), 89.3(5)
Ru(1)–C(1*m*)–O(1*m*)	177(1), 174.7(9)	177.4(8), 178(1)
Ru(2)–C(2*m*)–O(2*m*)	176(1), 176.5(9)	178.2(9), 176.0(7)
Ru(3)–C(3*m*)–O(3*m*)	–	178.6(9), 179(1)

[a] Carbonyls C,O (n = 1–3) are attached to Ru(n) [n = 1, 2, (3)]; C,O [1, 2, (3)m] designate carbonyls m = 1, 2, (3) attached to Ru[1, 2, (3)].

The successful synthesis and structural determination of complex **4** gave another suitable complex containing Tl–Ru single bonds for comparison against that of **3** and as such will be discussed here. Complex **3** crystallises in the monoclinic centrosymmetric space group $P2_1/c$, a single formula unit, devoid of crystallographic symmetry, comprising the asymmetric unit of the structure. The structure of **3** comprises an essentially one-dimensional polymeric strand with a repeating unit consisting of one cation and one anion. The close contact of a fluorine atom from the tetrafluoroborate anion of the repeating unit and that of an adjacent repeating unit with the thallium atom of the cation [2.88(1), 2.92(1) Å] results in the observed polymeric structure. The anion B–F(1–4) are 1.38, 1.39, 1.32, 1.34(2) Å, suggesting a distinction between the interacting and non-interacting F–B distances, but that may be impacted by lack of libration correction. F(1)–B–F(2) and F(3)–B–F(4) are enlarged above the tetrahedral norm to 112(1), 120(2)°.

The cation comprises two $\{Ru(CO)_2(\eta\text{-}C_5H_5)\}$ groups coordinated to a central thallium atom such that the Ru–Tl–Ru vector is essentially linear [176.98(3) °]. The geometries about the two Ru atoms are unremarkable but the relative synclinal orientation of the fragments is intriguing given that this stereochemistry places the two cyclopentadienyl ligands at the intuitively unfavourable point of least separation. Presumably the steric requirements of the cations is such that this orientation offers the most favourable crystal packing situation as well as allowing the maximum intermolecular anion-cation contacts. The Tl–Ru bond lengths of 2.6298(7) Å [Ru(1)] and 2.6260(7) Å [Ru(2)] seem unusually "short" in comparison to the sum of the two metallic radii (3.05 Å).[33] However, a recent structural determination of a similar complex, $[\{Ru(CO)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_9)\}_2(\mu\text{-}Tl)][NEt_4]$[31] gave a significantly shorter distance of 2.5994(4) Å. In this anionic complex the Ru–Tl–Ru vector is appreciably bent at 165.67(2)°.

The Tl_3Ru complex **4** crystallises in the centrosymmetric space group $P\bar{1}$; a single molecule, devoid of crystallographic symmetry, together with one half of the toluene molecule of solvation, which lies disordered about a crystallographic inversion centre, comprises the asymmetric unit of the structure. The molecular structure of **4** is shown in Figure 2, together with the numbering scheme used; pertinent bond lengths and angles are presented in Table 1.

The determination shows that the complex consists of a central thallium atom surrounded by three $\{Ru(CO)_2(\eta\text{-}C_5H_5)\}$ groups. The geometry about the thallium atom is trigonal planar, as is evident from the sum of the three ∠ Ru–Tl–Ru being equal to 360°, with the thallium atom located only 0.012(1) Å out of the Ru_3 plane. The measured Tl–Ru bond lengths are 2.7327(8) [Ru(1)], 2.7198(8) [Ru(2)] and 2.7089(8) Å [Ru(3)], which are significantly elongated from those measured for **3** by ca. 0.09 Å and 0.133 Å for **9** but "short" compared to the sum of the metallic radii.[33] The large steric bulk of the $\{Ru(CO)_2(\eta\text{-}C_5H_5)\}$ groups appears to be accommodated around the central thallium atom by rotation about the Tl–Ru vectors resulting in two of the cyclopentadienyl ligands orientated on the same side of the $TlRu_3$ plane with the remaining cyclopentadienyl ligand in a relative anticlinal orientation. The overall arrangement of the $\{Ru(CO)_2(\eta\text{-}C_5H_5)\}$ groups is comparable to that observed in the solid-state structure of the triiron thallium complex **8**;[28] presumably the Tl–Ru bond rotations play some part in the solution process which results in the equivalence observed in the ^1H and ^{13}C NMR solution spectra. Similar rotation about the M–Ga vectors of $[\{M(CO)_3(\eta\text{-}C_5H_5)\}_3(\mu_3\text{-}Ga)]$ (M = Mo **5**,[40] W **6**[41]) has been discussed previously.[42] The (carborane)$Ru(CO)_2$ units in **9** are mutually twisted and seem to allow even closer approach of the Ru and Tl centres.

With these observations in mind, elongation of the Tl–Ru bond lengths for **4** with respect to **3** and **9** may only be consequent on the steric congestion about the thallium atom and not on the presence of any multiple bonding in complex **3**. This situation is a reminder that the assignment of multiple bonding in these and other systems, based purely on structural data, is fraught with uncertainty.

Quantum Chemical Calculations of $[\{Ru(CO)_2(\eta\text{-}C_5H_5)\}_2(\mu\text{-}Tl)(F\text{–}BF_2\text{–}F)]_\infty$ (3)

In order to probe the nature of the bonding in **3**, quantum-chemical calculations were performed on $[\{Ru(CO)_2(Cp)\}_2Tl]^+$ at the geometry observed from the single-crystal X-ray structural determination of **3** to obtain the total charge density distribution, $\rho(r)$, for analysis using the theory of Atoms in Molecules (AIM).[43] To produce $\rho(r)$ amenable to study by AIM, all electron basis sets were used in conjuction with the Hartree–Fock method.

Within the theory of AIM, bonds are defined in terms of lines of maximum charge density connecting given nuclei, such that each line passes through a saddle point. The collection of these bond paths as well as other topological features of $\rho(r)$ is termed the molecular graph. For **3** the molecular graph is comprised of 2 Ru–Tl, 14 Ru–C, 4 C–O, 10 C–C and 10 C–H bond critical points. As predicted, ring critical points were located at the centre of each cyclopentadienyl ring and cage critical points located between each ruthenium and cyclopentadienyl ligand. The location of these bond critical points indicated that the utilised basis sets were adequate for the purpose of describing the total ρ present within the solid-state structure of **3**. Bond critical point data are summarised in Table 2.

Table 2. Average values, in atomic units, of $\rho(r)$ and $\nabla^2\rho(r)$ at various bond critical points in **3**.

Bond	$\rho(r)$	$\nabla^2\rho(r)$
Ru–Tl	0.065	0.12
Ru–C (CO)	0.15	0.63
Ru–C (Cp)	0.079	0.22
C–O	0.45	0.56
C–C	0.27	–0.91

Inspection of $\rho(r)$ at the ruthenium and thallium bond critical points shows these values are relatively small and possess positive Laplacians [$\nabla^2\rho(r)$], also evident from Figure 3 is the depletion of charge in the Ru–Tl internuclear regions, tending to indicate that the charges of the ruthenium and thallium nuclei are contracted and best described as "closed shell" or ionic.[43] The interatomic surface separating the ruthenium and thallium atoms is also shown.

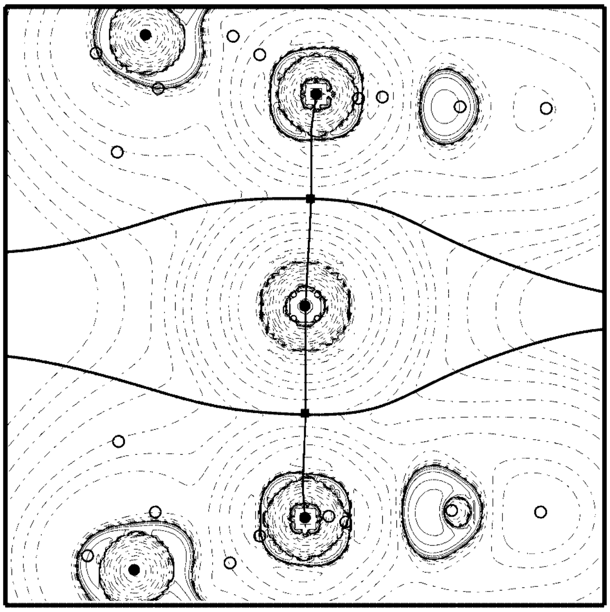

Figure 3. Plot of $\nabla^2\rho(r)$ for **3**, in a plane containing the metal nuclei. Full contours denote regions where charge is concentrated ($\nabla^2\rho(r) < 0$) and broken contours denote regions where charge is depleted ($\nabla^2\rho(r) > 0$). The bond paths joining the Ru and Tl nuclei are superimposed, and the bond critical point is denoted by the filled square. The interatomic surface separating Ru and Tl is also shown.

Similar depletion of charge in the internuclear region of a metal–metal bond has recently received experimental verification for the molecules $[Co_2(CO)_6(AsPh_3)_2]$[44] and $[Mn_2(CO)_{10}]$.[45]

Although the implied ionic nature of the Ru–Tl interaction suggested that multiple metal–metal bonding was absent in **3**, further clarification of the interaction by determination of the atomic populations for each metal nucleus was sought. Two separate methodologies were employed for these calculations:

1) integration of the calculated charge density within the zero-flux surface for each atom;[43]

2) use of the Natural Bond Orbital scheme (NBO).[46,47]

Atomic populations calculated by both methods are presented in Table 3 and support the initial calculations that the Ru–Tl bonding interaction is best described as ionic with no support for any metal–metal multiple bonding but there is substantial donation of electron density from the Ru atoms to the Tl centre. Importantly, the NBO analysis yields electron configurations of $6s^{1.5}$ $6p^{0.6}$ for thallium and $5s^{0.4}$ $4d^{7.4}$ for both ruthenium atoms. Thus, one can consider a dative interaction from the Ru to the Tl as a description of the bonding in **3**.

Table 3. Net atomic populations (q), calculated for both the experimental and optimised geometries of **3**.

Method				
	All electrons		B3LYP/LANL2DZ	
	Experimental geometry		0°	180°
q	Integrated	NBO	NBO	NBO
Tl	1.32[a]	0.74	1.03	1.03
Ru	0.16	0.16	–0.25	–0.25
CO	–0.10	0.07	0.16	0.15
Cp	–0.11	–0.17	–0.08	–0.07

[a] This value obtained by difference from the other integrated populations.

The observed synclinal orientation of the $\{Ru(CO)_2(\eta\text{-}C_5H_5)\}$ fragments in complex **3** was noted in the solid-state structure and so optimisation of this and the anticlinal stereochemistry was undertaken at the B3LYP/LANL2DZ level of theory. The calculated bond lengths and angles at these orientations were found to be closely similar to the experimental data (Table 4).

Surprisingly, the difference in energy of the two orientations was calculated at 5 kJ/mol, in favour of the anticlinal geometry, and one may have regarded that this orientation would be the most favoured based purely upon steric considerations. Observation of the synclinal stereochemistry in the solid-state structure, coupled with the rather small energy difference calculated between the syn- and anticlinal orientations, suggests that the stereochemistry may be purely a result of crystal packing effects or, perhaps, stabilisation by the tetrafluoroborate counter-anions. Additionally,

Table 4. Selected experimental and calculated bond lengths [Å] and angles (°) for **3**.

	Experimental	Calculated geometry 0°	Calculated geometry 180°
Bond length			
Tl–Ru	2.6279	2.743	2.740
Ru–C (CO)	1.875	1.898	1.897
Ru–C (Cp_c)	1.885	2.001	2.000
C–O	1.135	1.178	1.178
Bond angle			
Ru–Tl–Ru	176.98	177.97	180.00
Ru–C–O	175.98	178.50	176.70
Tl–Ru–C (CO)	88.23	88.98	89.20
Tl–Ru–C (Cp_c)	120.0	121.80	120.98
(CO) C–Ru–C (CO)	92.40	92.80	92.84
(Cp_c) C–Ru–C (CO)	122.5	126.50	126.70

NBO charges obtained for both optimised geometries also suggest that thallium is unipositive (see Table 3).

The chemistry which results in the formation of **3** can represented by the following equation:

$$2[RuCl(CO)_2(\eta\text{-}C_5H_5)] + 4Tl(BF_4)_4 \rightarrow [\{Ru(CO)_2(\eta\text{-}C_5H_5)\}_2(\mu_2\text{-}Tl)][BF_4] + 2TlCl + Tl(BF_4)_3$$

The reaction presumably proceeds by oxidation of thallous ions to give formally zero-valent ruthenium that then combines with the available Tl^+ ions to give the products. However, this intrepretation is a little problematic given that it suggests that highly oxidising Tl^{III} will co-exist with highly reduced ruthenium species.

Conclusions

We have shown that so-called simple halide abstraction reactions can be problematic but some TlRu complexes are readily prepared by nucleophilic substitution of transition metal halides. Ab initio calculations have helped rationalise both the bonding within the linear Ru–Tl–Ru complex and the observation of solid state packing effects within the crystal structure of complex, **3**, and suggesting that the Tl atom is a significant acceptor of electron density in the linear Ru–Tl–Ru complex. Additionally, it is clear that bond lengths alone are no arbiter of multiple bonding

Experimental Section

General Remarks: Manipulations of oxygen- and moisture-sensitive compounds were performed under high purity argon using standard Schlenk techniques or in a dry box (Miller Howe).

Infrared spectra were recorded with a Bio-Rad FTS 45 or 40 FTIR spectrometer. ^1H and ^{13}C NMR spectra were acquired with Varian Gemini 200 or Bruker ARX 500 spectrometers. ^{31}P NMR spectra were acquired with a Bruker ARX 500 spectrometer. ^1H and ^{13}C NMR spectra were referenced with respect to incompletely deuterated solvent signals. Mass spectra were obtained with a VG AutoSpec spectrometer employing a Fast Atom Bombardment (FAB) ionisation source in all samples unless otherwise specified. Elemental analyses were performed by The Research School of Chemistry Microanalytical Unit, Australian National University, ACT. *n*-Hexane and toluene were dried with sodium metal and distilled from sodium benzophenone ketyl under argon. Distilled solvents were stored over sodium or potassium mirrors until use.

$[\{Ru(CO)_2(\eta\text{-}C_5H_5)\}_2(\mu\text{-}Tl)][BF_4]$(3): A solution of $RuCl(CO)_2(\eta\text{-}C_5H_5)$ (100 mg, 0.388 mmol) and $TlBF_4$ (112 mg, 0.385 mmol) in tetrahydrofuran (30 mL) was heated at reflux (48 h) till the infrared absorption at 2023 cm^{-1} became constant. The reaction mixture was filtered, the solution volume reduced (to ca. 20 mL), then added dropwise to diethyl ether (50 mL) to give a pale yellow precipitate. Recrystallisation (CH_2Cl_2/Et_2O) gave **3** (60 mg, 42%) as yellow rods. $C_{14}H_{10}BF_4O_4Ru_2Tl$ (735.56): calcd. C 21.85, H 1.37; found C 22.21, H 0.83. FABMS: *m/z* (%) = 651 (35) [M^+]. IR (CH_2Cl_2): $\tilde{\nu}$ = 2024 (m), 1999 (m), 1971 [m (CO)] cm^{-1}. ^1H NMR (500 MHz, [D_6]acetone, 25 °C): δ = 5.54 [s, (η-C_5H_5)] ppm. ^{19}F NMR (470 MHz, [D_6]acetone, 25 °C): δ = 151.7 (s, BF_4) ppm.

$[\{Ru(CO)_2(\eta\text{-}C_5H_5)\}_3(\mu\text{-}Tl)]$(4)·$0.5C_6H_5CH_3$: A solution of freshly prepared $Na[Ru(CO)_2(\eta\text{-}C_5H_5)]$ (0.674 mmol) in tetrahydrofuran was added to a stirred solution of $TlCl_3$ (70 mg, 0.224 mmol) in tetrahydrofuran (15 mL), then heated at reflux (2 h). The solvent was removed in vacuo and the residues extracted with toluene (2 × 30 mL) to give a blood-red solution. Reduction of the solution volume (to ca. 50 mL) and addition of hexane gave red crystals of **4** at –35 °C (119 mg, 61%). IR (C_7H_7): $\tilde{\nu}$ = ν(CO) = 1998 m, 1972 (s), 1929 [m (CO)] cm^{-1}. ^1H NMR (200 MHz, [D_6]benzene, 25 °C): δ = 4.69 [d, $^2J_{TlH}$ = 7.9 Hz, (η-C_5H_5)] ppm. ^{13}C NMR (50.3 MHz, [D_6]benzene, 25 °C): δ = 202.7 (d, $^2J_{TlC}$ = 279.3 Hz, Ru-CO), 85.1 [d, J_{TlH} = 7.8 Hz, (η-C_5H_5)] ppm. FABMS: *m/z* (%) = 651 (35) [M^+ – {$Ru(CO)_2(\eta\text{-}C_5H_5)$}]. $C_{21}H_{15}O_6Ru_3Tl$ (871.24): calcd. C 28.95, H 1.74; found C 28.39, H 1.67.

X-ray Crystallographic Study: Full spheres of CCD area-detector diffractometer data were measured (Bruker AXS instrument, ω-scans, *T* ca. 300 K; monochromatic Mo-K_α radiation, $\lambda = 0.7107_3$ Å) yielding $N_{t(otal)}$ reflections, these merging to *N* unique (R_{int} quoted) after "empirical"/multiscan absorption correction (proprietary software). N_o with $F > 4\sigma(F)$ were considered "observed"

Table 5. Crystallographic structure determinations of $[\{Ru(CO)_2(\eta\text{-}C_5H_5)\}_2(\mu\text{-}Tl)][BF_4]$ (**3**) and $[\{Ru(CO)_2(\eta\text{-}C_5H_5)\}_3(\mu\text{-}Tl)]$ (**4**).

Compound	3	4
Formula	$C_{14}H_{10}BF_4O_4Ru_2Tl$	$C_{24.5}H_{19}O_6Ru_3Tl$
M_r	735.56	917.01
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
a [Å]	12.023(1)	7.5367(4)
b [Å]	12.996(1)	9.6907(5)
c [Å]	13.163(1)	18.841(1)
α [°]	–	94.321(4)
β [°]	113.239(1)	95.88(1)
γ [°]	–	104.672(1)
V [$Å^3$]	1889.9(5)	1316.8(1)
$D_{calcd.}$ [$g\,cm^{-3}$]	2.585	2.312
Z	4	2
μ_{Mo} [cm^{-1}]	101.4	78.2
Dimension [mm]	0.20 × 0.10 × 0.08	0.45 × 0.22 × 0.08
$T_{min./max.}$	0.59	0.47
$2\theta_{max.}$ [°]	58	58
N_t	21923	14368
$N(R_{int})$	4772(0.036)	6376(0.046)
N_o	3681	5813
R	0.043	0.038
R_w	0.062	0.041

and used in the full-matrix least-squares refinements, refining anisotropic thermal parameter forms for the non-hydrogen atoms $(x, y, z, U_{iso})_H$ being constrained at estimated values. Conventional residuals R, R_w on $|F|$ are cited at convergence {reflection weights: $[\sigma^2(F) + 0.0004F^2]^{-1}$}. Neutral atom complex scattering factors were employed within the Xtal 3.7 program system.[48] Pertinent data are given in Table 5 and Figure 1 and Figure 2, the latter showing 20% probability amplitude displacement envelopes for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å.

CCDC-116532 and -116533 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Theoretical Calculations: Ab initio calculations were performed with the Gaussian 94 software package.[49] The experimental geometry was used for the calculation of a Hartree–Fock all-electron wave function. The Huzinaga[50] basis sets with uncontracted outer d-shells were used for Ru [432211/4211/321] and Tl [4322211/422211/4211/3] while standard 3-21G basis sets[49] were used for C, O and H atoms. Optimized geometries were obtained using the B3LYP functional[51,52] as implemented in Gaussian 94[49,53] in conjunction with the LANL2DZ effective core potentials for Ru and Tl[54] and D95V all-electron basis sets[55] for C,O and H. The MORPHY98 program[56] was used to search for critical points in the total charge density[57] and to calculate integrated atomic populations.[58] Orbital occupancies and charges were also obtained using the natural bond orbital (NBO) program[46,47] implemented in Gaussian 94.

Acknowledgments

C. S. G. was the holder of a Australian Postgraduate Award.

---

[1] A. Hamel, N. W. Mitzel, H. Schmidbaur, *J. Am. Chem. Soc.* **2001**, *123*, 5106.
[2] H. Schmidbaur, *Gold. Bull.* **2000**, *33*, 3.
[3] P. Pyykko, W. Schneider, A. Bauer, A. Bayler, H. Schmidbaur, *Chem. Commun.* **1997**, 1111.
[4] H. Schmidbaur, A. Hamel, N. W. Mitzel, A. Schier, S. Nogai, *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 4916.
[5] Q.-M. Wang, Y.-A. Lee, O. Crespo, J. Deaton, C. Tang, H. J. Gysling, M. C. Gimeno, C. Larraz, M. D. Villacampa, A. Laguna, R. Eisenberg, *J. Am. Chem. Soc.* **2004**, *126*, 9488.
[6] E. J. Fernandez, A. Laguna, J. M. Lopez-De-Luzuriaga, M. Monge, P. Pyykko, N. Runeberg, *Eur. J. Inorg. Chem.* **2002**, 750.
[7] V. W.-W. Yam, K. M.-C. Wong, N. Zhu, *Angew. Chem. Int. Ed.* **2003**, *42*, 1400.
[8] V. W.-W. Yam, *C. R. Chim.* **2005**, *8*, 1194.
[9] S. Aldridge, *Angew. Chem. Int. Ed.* **2006**, *45*, 8097.
[10] C. S. Griffith, G. A. Koutsantonis, B. W. Skelton, A. H. White, *Chem. Commun.* **1998**, *7*, 1805.
[11] L. T. Byrne, J. P. Hos, G. A. Koutsantonis, B. W. Skelton, A. H. White, *J. Organomet. Chem.* **2000**, *598*, 28.
[12] C. S. Griffith, G. A. Koutsantonis, B. W. Skelton, A. H. White, *Chem. Commun.* **1998**, 1805.
[13] L. T. Byrne, C. S. Griffith, J. P. Hos, G. A. Koutsantonis, B. W. Skelton, A. H. White, *J. Organomet. Chem.* **1998**, *565*, 259.
[14] L. T. Byrne, C. S. Griffith, G. A. Koutsantonis, B. W. Skelton, A. H. White, *J. Chem. Soc., Dalton Trans.* **1998**, 1575.
[15] C. S. Griffith, G. A. Koutsantonis, B. W. Skelton, A. H. White, *J. Organomet. Chem.* **2003**, *670*, 198.
[16] C. S. Griffith, G. A. Koutsantonis, B. W. Skelton, A. H. White, *Chem. Commun.* **2002**, 2174.
[17] L. T. Byrne, J. P. Hos, G. A. Koutsantonis, B. W. Skelton, A. H. White, *J. Organomet. Chem.* **1999**, *592*, 95.
[18] C. S. Griffith, G. A. Koutsantonis, B. W. Skelton, A. H. White, *Angew. Chem. Int. Ed.* **2005**, *44*, 3038.
[19] C. S. Griffith, G. A. Koutsantonis, B. W. Skelton, A. H. White, *J. Organomet. Chem.* **2005**, *690*, 3410.
[20] D. L. Reger, C. J. Coleman, *J. Organomet. Chem.* **1977**, *131*, 153.
[21] M. Rosenblum, *Acc. Chem. Res.* **1974**, *7*, 122.
[22] A. S. Batsanov, O. S. Manole, Y. T. Struchkov, G. P. Zol'nikova, D. N. Kravtsov, *Metalloorg. Khim.* **1993**, *6*, 213.
[23] A. Jungbauer, H. Behrens, *Z. Naturforsch., Teil B* **1978**, *33*, 1083.
[24] T. Blackmore, M. I. Bruce, F. G. A. Stone, *J. Chem. Soc. A* **1968**, 2158.
[25] J. C. Calabrese, L. M. Clarkson, T. B. Marder, N. C. Norman, N. J. Taylor, *J. Chem. Soc., Dalton Trans.* **1992**, 3525.
[26] J. Burlitch, T. W. Theyson, *J. Chem. Soc., Dalton Trans.* **1974**, 828.
[27] J. Rajaram, J. A. Ibers, *Inorg. Chem.* **1973**, *12*, 1313.
[28] J. W. v. Hal, L. B. Alemany, K. H. Whitmire, *Inorg. Chem.* **1997**, *36*, 3152–3159.
[29] B. Walther, R. Mahrwald, C. Jahn, W. Klar, *Z. Anorg. Allg. Chem.* **1976**, *423*, 144.
[30] B. Walther, C. Rockstroh, *J. Organomet. Chem.* **1972**, *44*, C4.
[31] J. C. Jeffery, P. A. Jelliss, Y.-H. Liao, F. G. A. Stone, *J. Organomet. Chem.* **1998**, *551*, 27.
[32] A. L. Balch, J. K. Nagle, M. M. Olmstead, P. E. Reedy Jr, *J. Am. Chem. Soc.* **1987**, *109*, 4123.
[33] A. F. Wells, *Structural Inorganic Chemistry*, 5th edn. ed., Clarendon Press, Oxford, **1984**.
[34] W. A. Herrmann, H.-J. Kneuper, E. Herdweck, *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 1062.
[35] W. A. Herrmann, *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 56.
[36] W. A. Herrmann, H.-J. Kneuper, E. Herdweck, *Chem. Ber.* **1989**, *122*, 445.
[37] W. Gade, E. Weiss, *J. Organomet. Chem.* **1981**, *213*, 451.
[38] B. Schiemenz, G. Huttner, *Angew. Chem. Int. Ed. Engl.* **1993**, *105*, 1840.
[39] G. B. Ansell, M. A. Modrick, J. S. Bradley, *Acta Crystallogr., Sect. C* **1984**, *40*, 1315.
[40] L. M. Clarkson, W. Clegg, D. C. R. Hockless, N. C. Norman, T. B. Marder, *J. Chem. Soc., Dalton Trans.* **1991**, 2229.
[41] A. J. Conway, P. B. Hitchcock, J. D. Smith, *J. Chem. Soc., Dalton Trans.* **1975**, 1945.
[42] R. M. Campbell, L. M. Clarkson, W. Clegg, D. C. R. Hockless, N. L. Pickett, N. C. Norman, *Chem. Ber.* **1992**, *125*, 55.
[43] R. F. W. Bader, *Atoms in Molecules: A Quantum Theory*, Oxford University Press, Oxford, **1990**.
[44] P. Macchi, D. M. Proserpio, A. Sironi, *J. Am. Chem. Soc.* **1998**, *120*, 13429.
[45] R. Bianchi, G. Gervasio, D. Marabello, *Inorg. Chem.* **2000**, *39*, 2360.
[46] E. D. Glendening, A. E. Reed, J. E. Carpenter, F. Weinhold, NBO 3.1, **1995**.
[47] A. E. Reed, L. A. Curtis, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899.
[48] S. R. Hall, D. J. du Boulay, R. Olthof-Hazekamp, *Xtal 3.7 User's Manual*, University of Western Australia, **2001**.
[49] M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, *Gaussian94*, Rev. B.1, Gaussian Inc., Pittsburgh, **1995**.

[50] J. Andzelm, S. Huzinaga, M. Klobukowski, E. Radzio-Andzelm, Y. Sakai, H. Tatewaki, *Gaussian Basis Sets for Molecular Calculations*, Elsevier, Amsterdam, **1984**.
[51] A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098.
[52] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B: Condens. Matter* **1988**, *37*, 785.
[53] P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Fisch, *J. Phys. Chem.* **1994**, *98*, 11623.
[54] P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 299.
[55] T. H. Dunning Jr, P. J. Hay, *Modern Theoretical Chemistry*, Plenum, New York, **1976**.
[56] P. L. A. Popelier, R. G. A. Bone, *MORPHY98*, A Topological Analysis Program, UMIST.
[57] P. L. A. Popelier, *Comput. Phys. Commun.* **1996**, *93*, 212.
[58] P. L. A. Popelier, *Mol. Phys.* **1996**, *87*, 1169

Received: January 9, 2007