pendence is exactly reproduced with a zero-field splitting (ZFS) of ^3B_g by 5 cm^{-1}. This splitting is correlated with the ZFS in the ground state as follows. In a Ti^{2+} single ion the $^3A_{2g}$ ground state has a ZFS D_c = 4.7 cm^{-1} into an A_{1g} (lower) and an E_g (higher) spinor component (D_{3d}).[8] In the dimer this zero-field splitting now occurs in the excited-state $^3A_{2g}{}^1E_g$, giving rise to the observed temperature dependence. In the dimer ground-state $^3A_{2g}{}^3A_{2g}$ the ZFS of the S = 1 level D_1 can be correlated with the single-ion value D_c by the following formula:[18]

$$D_1 = -D_c + 3D_e \tag{9}$$

where D_e arises from anisotropic exchange and dipole-dipole interactions. In an exchange-coupled dimer of Cr^{3+}, D_e was found to provide a negligible correction for D_c.[19] Assuming the same to be true here, the ZFS in the S = 1 dimer ground state has thus approximately the same value as in the dimer excited state but with opposite sign. This is indeed borne out by our experiments. As a result of the $\Delta M_S = 0$ selection rule for an exchange mechanism, only two transitions are allowed, with an energy difference of $|D_1| + |D_c|$ = 10 cm^{-1}; see Figure 4. The observed 11-cm^{-1} splitting of the dimer emission lines 1a and 1b is in excellent agreement with this.

The hot lines 1c and 1d in the 33 K spectrum of Figure 3 are assigned to transitions from the higher rhombic component of the *gerade* emitting state to the ^3A_u ground state. The temperature dependence is consistent with an excited-state splitting of 95 cm^{-1}, corresponding to the energy separation between 1a,b and 1c,d. The ^3A_g-^3B_g splitting is thus considerably larger than the corresponding splitting of 12.5 cm^{-1} in Ti^{2+}Mn^{2+} dimers.[11] We attribute this difference to the larger ionic radius of Ti^{2+} causing a stronger lattice distortion. In addition the higher covalency within Ti-Cl-Ti may contribute to this splitting.

No transitions to the singlet and quintet levels of the $^3A_{2g}{}^3A_{2g}$ ground state are observed. This is in contrast to Ti^{2+}Mn^{2+} dimers in MgCl$_2$[11] and to all the systems of exchange-coupled Cr^{3+} ions that have been studied by optical spectroscopy. We are therefore unable to directly determine the exchange splitting of the Ti^{2+} dimer ground state by optical spectroscopy. The fact that the $\Delta S = \pm 1$ dimer transitions are at least 2 orders of magnitude weaker than the $\Delta S = 0$ transitions is in good agreement with our conclusion that the antiferromagnetic coupling is very strong ($-2J \geq 100$ cm^{-1} in the triangular trimers). The Tanabe intensity mechanism is absolutely dominant for the dimer and trimer transition, and a careful examination of this mechanism shows that both the exchange parameters J and the intensity coefficients Π derive their strength from the same one-electron-transfer integrals.[20] This can in turn be correlated with the covalency of the M^{2+}-Cl$^-$ bond, which is stronger for Ti^{2+}-Cl$^-$ than for any other divalent 3d transition-metal ion. TiCl$_2$ is black, indicating a rather low-lying conduction band, whereas all the other chlorides of divalent 3d ions are transparent. Small values of both the molar volume[3] and the magnetic susceptibility[6] of TiCl$_2$ reflect the high covalency of the Ti-Cl-Ti bonds and thus the strongly antiferromagnetic Ti^{2+}-Ti^{2+} exchange interaction.

4.4. Emission from Ti^{2+} Trimers. The most intense luminescence lines of linear and bent trimer chains are T$_1$ and T$_2$ at 7450 and 7467 cm^{-1}, respectively. They correspond to transitions to the $^3A_{2g}{}^3A_{2g}{}^3A_{2g}$ ground-state configuration. As shown in the lower part of Figure 5, there is only one ground-state level with S = 0, in contrast to the numerous S = 1 and S = 2 levels. Since only one line for each species is observed, we conclude that the emission is due to a transition from an S = 0 level of the $^3A_{2g}{}^3A_{2g}{}^1E_g$ singly excited state to the $|1,0\rangle$ ground-state level. The exchange splitting pattern of $^3A_{2g}{}^3A_{2g}{}^1E_g$ is expected to correspond to the $^3A_{2g}{}^3A_{2g}$ dimer ground-state splitting, the lowest level having S = 0. In contrast to the dimer emission lines, the trimer emission lines are not split by a second-order spin-orbit interaction. This nicely confirms their assignment to $S = 0 \rightarrow S = 0$ transitions.

The features around 6500 cm^{-1} in Figure 2C are assigned to transitions to the singly excited trimer ground state $^3A_{2g}{}^3A_{2g}{}^3E_g$. As in the dimers, there is a resonance splitting of this state, and we only observe transitions to one component. All other trimer transitions are assumed to occur at energies below 6000 cm^{-1}, which is out of range of the near-IR detector used in this study. In contrast to dimers there is a resonance splitting of the $^3A_{2g}{}^3E_g{}^3E_g$ doubly excited trimer ground state, which explains the absence of trimer lines around 6100 cm^{-1}. Transitions to the triply excited trimer ground states $^3E_g{}^3E_g{}^3E_g$ are expected to occur around 5250 cm^{-1}.

All trimer lines are shifted by about 100 cm^{-1} to lower energy relative to the corresponding dimer lines, due to smaller electron repulsion parameters. This is the result of increasing delocalization of the unpaired electrons, going from single ions to dimers to trimers.

Acknowledgment. This work was financially supported by the Swiss National Science Foundation.

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Metal-Metal Bonds in Tl(I)-Tl(I) Compounds: Fact or Fiction?

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Until recently, Tl-Tl interactions have been generally regarded as weak and have been postulated on the basis of vibrational and X-ray measurements on some inorganic Tl(I) compounds.[1,2] In contrast, element-element bonds in inorganic and organometallic compounds of B, Al, Ga, and In are well-known. However, Schumann and co-workers[3] recently obtained (η^5-pentabenzylcyclopentadienyl)thallium(I), (η^5-(C$_6$H$_5$CH$_2$)$_5$C$_5$)Tl, in dimeric form in the solid state with a Tl-Tl distance of 3.632 Å and a ring-center-Tl1-Tl2 angle α of 131.8°. Most CpTl derivatives crystallize in polymeric zigzag chains, containing alternating Tl atoms and Cp rings. Schumann et al. concluded that the distance between the two thallium atoms is far too large for a conventional metal-to-metal bond. Moreover, the CpM compounds (M = In, Tl) so far studied are monomeric in solution, which suggests that the interaction is weak. However, Janiak and Hoffmann[4] have

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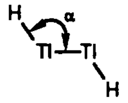
Table I. Calculated Bond Distances r_e in Å, Force Constants k_e in mdyn/Å and Dissociation Energies D_e in kJ/mol for the Molecule TlH (Zero-Point Vibration Not Included)[a]

		HF	MP2	MP3	MP4	CISD	CISC	QCI	exptl	ref 17
r_e	NR	1.922	1.924	1.929	1.932	1.932	1.934	1.934		
	R	1.893	1.899	1.906	1.910	1.910	1.913	1.912	1.870	1.99
k_e	NR	1.346	1.299	1.265	1.242	1.242	1.222	1.221		
	R	1.198	1.162	1.128	1.105	1.099	1.078	1.078	1.143	0.99
D_e	NR	197.9	241.7	253.9	257.5	252.2	257.4	259.1		
	R	163.1	227.6	240.8	244.9	241.4	245.8	246.8		
	R/SO	104.0	165.5	178.7	182.2	179.3	184.2	184.7	198	175

[a] The relativistic spin-orbit (SO) correction is taken from ref 11 (RHF, 59.1 kJ/mol; exptl, 62.1 kJ/mol). Experimental values are from ref 15. Reference 17 gives spin-orbit-coupled relativistic CI pseudopotential calculations by Christiansen et al.

recently published extended Hückel calculations on the model compound Tl_2H_2 (**1**) and have concluded that there is a strong



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Tl–Tl bond at an angle of about α(H–Tl–Tl) = 120°. On the other hand, extended Hückel calculations on dimeric CpIn by Budzelaar and Boersma[5] indicate that there are only weak interactions between the two indium atoms. The origin of the H–Tl–Tl–H "bonding" angle of between 110 and 120° was stated to be due to avoidance of strong repulsions between the lone pairs on the metal atoms.[5]

The separation between the metal atoms in the isostructural compounds $(C_6H_5CH_2)_5C_5M$ (M = In, Tl) are almost identical (3.63 Å).[6,7] Indium is known to form more stable bonds in its compounds than does thallium,[1,2] so we would expect the intermetallic distance to be less in $(C_6H_5CH_2)_5C_5In$ than in $(C_6H_5CH_2)_5C_5Tl$. Compare, for example, the dimers Tl_2 and In_2. Tl_2 is weakly bound with a bond distance somewhere between 3.5 and 3.7 Å and a dissociation energy of about 30 kJ/mol.[2,8] On the other hand, In_2 is quite stable with a bond distance of 3.1 Å and a dissociation energy of about 80 kJ/mol.[9] This must raise doubts about the existence of a Tl–Tl bond in $[(C_6H_5CH_2)_5C_5Tl]_2$ and Tl_2H_2. There may be other interactions that are responsible for the fact that $(C_6H_5CH_2)_5C_5Tl$ crystallizes in a dimeric form. Moreover, extended Hückel calculations may not be very reliable for calculating molecular properties in heavy-element compounds where relativistic effects become increasingly important. It is well-known that even bond distances are not well described by the semiempirical extended Hückel method.[10] For small molecules like Tl_2H_2, however, sophisticated methods, like configuration interaction including relativistic effects via relativistic pseudopotentials, are now feasible.

In order to investigate the nature of the Tl(I)–Tl(I) interaction in Tl_2H_2, CI (configuration interaction) calculations for TlH and Tl_2H_2 have been performed. Relativistic pseudopotentials, adjusted to Dirac–Fock ionization potentials, and extensive basis sets have been used, as described in ref 11. Since relativistic effects are very important for thallium compounds,[12] we also performed correlated nonrelativistic and relativistic SCF calculations for TlH. The different levels of approximations used are Hartree–Fock (HF), Møller-Plesset (MP) up to the fourth order (MP2-4), configuration interactions with single and double substitutions (CISD) including size-consistency correction (CISC), and size-consistent quadratic configuration interaction (QCISD(T), which will be abbreviated to QCI).[13,14] The H–Tl–Tl–H torsion angle is fixed at 180° (trans-bent structure). The basis set superposition errors are below 1 kJ/mol at the HF level. The results for TlH are shown in Table I. Best results are obtained at the QCI level, as expected. If we include the molecular contribution of the spin–orbit coupling, i.e. Δ_M = 5.7 kJ/mol,[11] the total spin–orbit corrected QCI dissociation energy is 190.4 kJ/mol and is in very good agreement with the experimental value (198 kJ/mol). The relativistic bond contraction is about 2 pm for TlH, smaller than previously published values for this molecule.[12,16,17] The agreement between the results for TlH and the experimental data therefore suggest that results of equally high quality should be obtainable for Tl_2H_2.

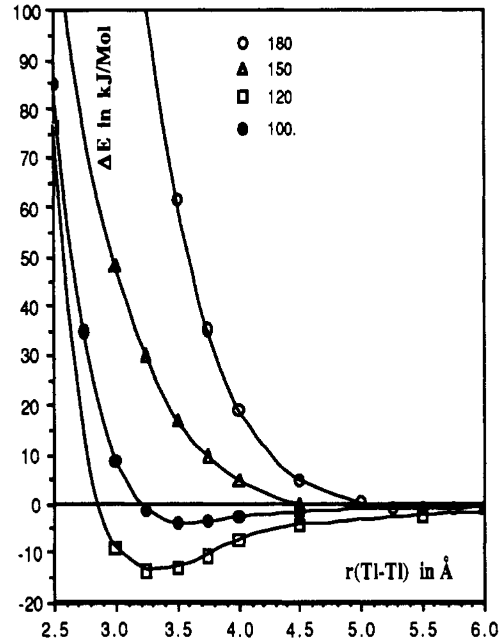

Figure 1. QCI $E(r,\alpha)$ potential curves for Tl_2H_2 in kJ/mol at a fixed Tl–H distance of 1.9 Å. r is the Tl–Tl distance in Å, α is the trans bent H-Tl-Tl angle in deg. The zero-line represents the dissociation limit of $Tl_2H_2 \rightarrow 2TlH$.

The potential curves for Tl_2H_2 at various H–Tl–Tl angles are shown in Figures 1 and 2. For the linear molecule (α = 180°) only a very shallow minimum about 5.6 Å was obtained, which is 0.9 kJ/mol below the dissociation limit ($Tl_2H_2 \rightarrow 2TlH$). At 3.632 Å (the observed Tl–Tl distance in $[(C_6H_5CH_2)_5C_5Tl]_2$), the Tl(I)–Tl(I) interaction is repulsive to the extent of 46 kJ/mol.

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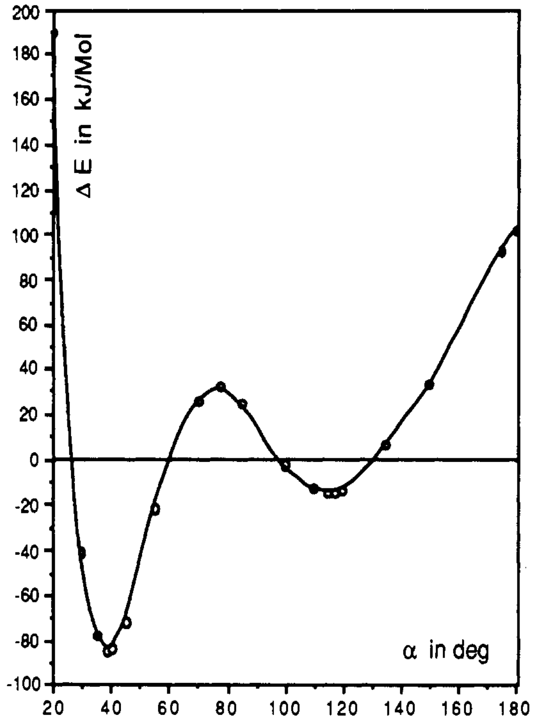


Figure 2. QCI $E(\alpha)$ potential curves for Tl_2H_2 in kJ/mol at fixed Tl–H and Tl–Tl distances of 1.9 and 3.25 Å, respectively. α is the trans bent H–Tl–Tl angle in deg. The zero-line represents the dissociation limit of $Tl_2H_2 \rightarrow 2TlH$.

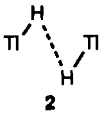
Table II. HF Mulliken Population Analysis and Orbital Energies (eV) for TlH and Tl_2H_2 (r(Tl–H) = 1.9 Å; r(Tl–Tl) = 3.25 Å)[a]

	TlH(NR)	TlH	Tl_2H_2 (α = 180°)	Tl_2H_2 (α = 115°)	Tl_2H_2 (α = 38.75°)
Tl(q)	0.45	0.43	0.46	0.40	0.51
Tl(6s)	1.80	1.86	1.78	1.78	1.86
Tl($6p_x$)	0.72	0.72	0.65	0.62	0.43
Tl($6p_y$)	0.0	0.0	0.0	0.18	0.20
$\epsilon(2a_g)$	-7.242	-7.723	-5.834	-7.260	-6.917
$\epsilon(2b_u)$			-9.174	-8.618	-9.928
$\epsilon(1a_g)$	-12.284	-13.692	-13.206	-13.288	-11.389
$\epsilon(1b_u)$			-14.381	-14.749	-16.773

[a] The C_2 axis defines the z direction, the Tl–Tl bond the x direction. q is the gross atomic charge ($Tl^{+q}H^{-q}$). If not otherwise specified, all calculations are carried out at the relativistic level.

To avoid such larger repulsive forces, the linear H–Tl–Tl–H arrangement moves into the more stable trans-bent structure with a bond angle α(H–Tl–Tl) of 115.1°. This minimum is about 14 kJ/mol below the dissociation limit (Figure 1). To ensure that the trans-bent Tl_2H_2 molecule represents a local minimum, the H–Tl–Tl–H torsion angle has been varied. A 5° change in the torsion angle resulted in an increase in energy of about 0.02 kJ/mol. The Tl_2H_2 trans-bent structure was also postulated recently by Janiak and Hoffmann[4] as well as Budzelaar and Boersma[5] using extended Hückel calculations. A possible explanation in terms of orbital interactions (Tl sp hybridization) was given by these authors. These findings agree qualitatively with the HF results reported here (compare the orbital energies in Table II with the one given in ref 4). However, the orbital energies for isolated TlH do not differ very much from the bent Tl_2H_2 arrangement at α = 115° (Table II). The calculations show that dramatic changes in orbital energies occur only for linear Tl_2H_2 (α = 180°) due to strong repulsive forces between the two thallium atoms. It may be interesting to compare the Mulliken population analyses for the different structures, also given in Table II. For TlH the orbital populations do not change dramatically due to relativistic effects. The Tl s orbital for all listed structures is almost inert (Tl(6s) ~ 2). As expected, the Tl($6p_y$) population increases and the Tl(6s) population decreases as α decreases, as found and discussed by Janiak and Hoffmann.[4] However, the estimation of bond stabilities from orbital pictures or population analyses is not adequate for discussing weak interactions, as occur in Tl_2H_2 (and will therefore not be discussed in detail).

The calculated QCI Tl–Tl distance at 115.1° is 3.28 Å, the Tl–H distance 1.894 Å. Hence, the Tl–H bond distance decreases slightly due to the interaction of the two TlH molecules. Note that the minima shown in Figure 1 are all very shallow. The Tl–Tl stretching force constant is below 1 mdyn/Å.[18] To see if this local minimum represents a "bond" (within the Born–Oppenheimer approximation), a frequency analysis[19] for Tl_2H_2 has been performed within the point group C_{2h} by using diagonal harmonic QCI force constants (in cm^{-1}): between 50 and 100 (Tl–Tl stretch); 342 (H–Tl–Tl bent); 1383 (Tl–H stretch). The very small splittings in the symmetric (A_g) and asymmetric (B_g) modes were neglected since nondiagonal force constants were not included in the frequency analysis. The frequency for the Tl–H stretch in isolated TlH at the QCI level is 1351 cm^{-1} (experimental 1391 cm^{-1}).[15] The difference in the total zero-point vibrations according to the dissociation $Tl_2H_2 \rightarrow 2TlH$ is therefore about 400 cm^{-1} or 5 kJ/mol. Hence, the zero-point vibration contribution to the energy is smaller than the dissociation energy of 14 kJ/mol. The dimer Tl_2H_2 should therefore be observable by low-temperature matrix isolation spectroscopy. Extended Hückel calculations by Janiak and Hoffmann[4] resulted in a nonbonding situation for the H-bridged geometry (**2**). This does not agree with the CI calculations (Figure 2); i.e., a second, deeper minimum at a lower angle of α = 38.75° follows the local minimum discussed above with exact D_{2h} symmetry at the minimum. This is because the H atoms now interact with two Tl atoms and probably is also due to an increased H–H interaction (the reaction $2TlH \rightarrow 2Tl + H_2$ is exothermic at 0 K with an enthalpy of -42 kJ/mol,[15] neglecting the zero-point vibration). The minimum at about 39° lies at -84.7 kJ/mol relative to the dissociation products TlH. This value is much lower than -42 kJ/mol. Note that the H–H distance in **2** is 2.396 Å, much longer than that in H_2 (0.741 Å). Hence, we can assume that structure **2** represents a stable form of dimeric TlH. The Tl_2 binding energy is assumed to be around 30 kJ/mol;[8] therefore, **2** may even represent the global minimum on the Tl_2H_2 hypersurface. At the MP2 level the optimized geometry is r(Tl–Tl) = 3.46 Å, r(Tl–H) = 2.12 Å, r(H–H) = 2.44 Å, and α(H–Tl–Tl) = 35.1°. A QCI calculation at this geometry yields ΔE = -108 kJ/mol (compare to Figure 2). However, for molecules like **2**, spin–orbit coupling may become important.[8] Also, such structures have not yet been observed in organothallium compounds, although ligand-bridged Tl species are known in inorganic compounds (see for example ref 20). This may be due to the small bonding interactions between two Cp rings, so **2** is not a good model to discuss interactions in $(CpTl)_2$ derivatives. Therefore, structure **2** has not been investigated in detail, but may certainly be interesting for gas-phase spectroscopic measurements on TlH. Also, the zero torsion angle corresponding to the reaction channel $Tl_2 + H_2 \rightarrow Tl_2H_2$ would be of interest.



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Even if Tl_2H_2 is bound at the QCI level, the Tl(I)–Tl(I) interaction is rather small. The main reason for the trans-bent

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(21) A Tl–Tl bond has been claimed by Wilkie and Oliver for $Tl_2(CH_3)_6^{2-}$, but attempts to prepare this compound by other authors failed (this compound is reported in many textbooks; see, for example: Coates, G. E.; Green, M. L. H.; Wade, K. *Organometallic Compounds*; Methuen & Co., Ltd.: London, 1982. See also the discussion in ref 2). Preliminary calculations on $Tl_2H_6^{2-}$ give no evidence so far for a Tl–Tl bond; calculations on $Tl_2(CH_3)_6^{2-}$ are underway.

structure in $[(C_6H_5CH_2)_5C_5Tl]_2$ is therefore expected to be the large repulsive forces between the $(C_6H_5CH_2)_5C_5Tl$ moieties in the linear R–Tl–Tl–R arrangement, as suggested by Budzelaar and Boersma,[5] rather than to be the Tl–Tl bond suggested by Janiak and Hoffmann.[4] Note also the very small Tl–Tl distance in Tl_2H_2 (3.28 Å) compared with $[(C_6H_5CH_2)_5C_5Tl]_2$ (3.63 Å). This suggests that other effects (e.g. steric effects) are present, which increase the Tl–Tl distance. Even the fairly short Tl–Tl internuclear distances in compounds like Tl_2SnO_3 (3.23 Å)[22] may be explained as being due to interactions of thallium with other atoms, e.g. the oxygen atom in the case of Tl_2SnO_3.[22] It is therefore unlikely that reasonably strong Tl(I)–Tl(I) bonds exist in any of the known inorganic or organometallic compounds of the element.[23] However, Tl(II)–Tl(II) bonds remain a possibility, especially in the solid state. Dronkowski and Simon[24] have recently reported the preparation of $Tl_{0.8}Sn_{0.6}Mo_7O_{11}$, which has a remarkably short Tl–Tl distance of 2.84 Å. A qualitative analysis suggested the presence of a single Tl–Tl bond between Tl^{2+} units, which may be stabilized by interaction with the oligomeric transition-metal clusters.[24]

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Registry No. $[\eta^5\text{-}(C_6H_5CH_2)_5C_5Tl]$, 109531-29-5; Tl, 7440-28-0.

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(23) A comparison of Figure 2 with the extended Hückel potential curve shown in ref 5 suggests that the extended Hückel method overestimates the interaction between two TlH molecules by at least a factor of 3. Therefore, only accurate quantum chemical procedures, such as the CI method,[24] using rather large basis sets to avoid basis set superposition errors, are able to describe weak interactions between two thallium atoms in thallium compounds. Note that the Tl–Tl interaction is repulsive at the HF level at all angles investigated; hence the weak Tl–Tl interaction is a correlation effect. Also, spin–orbit effects are very small for the HTl–TlH interaction and can be neglected.

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Thermochemical and Kinetic Studies of the Electron-Transfer Catalysis of Arene Replacement by $P(OMe)_3$ Ligands in (η^5-Cyclopentadienyl)(η^6-arene)iron(II) Cations

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In the field of organometallic chemistry, recent studies have shown that some reactions may be efficiently catalyzed by electron transfer[1,2] at electrodes or by redox chemical means. The systems most generally studied involve ligand replacement in mononuclear and polynuclear complexes. For all these reactions the key step is the labilization of intermediate paramagnetic species containing 17 or 19 electrons in the valence orbitals of one metal center.[3] A complete knowledge of the course of these catalyzed reactions requires kinetic studies in order to establish the mechanism (associative or dissociative) of the ligand substitution. These kinetic studies are generally performed by electrochemical means using a working curve[4] or simulated voltammograms,[5] but they do not take into account the interference of deactivation reactions.[6] In this paper, we report that calorimetric measurements carried out during a ligand substitution catalyzed by an electron transfer constitute the basis of a kinetic study of the reaction in homogeneous solution. In the same experiments the rate of deactivation steps may be obtained. Moreover, the example described shows, for the first time, that the electron-transfer catalysis may be used for thermochemical studies of chemical reactions that are otherwise unfeasible.

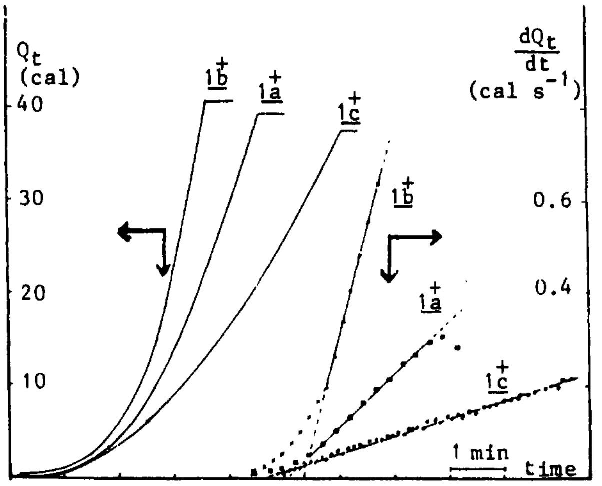

Figure 1. Thermograms of reaction 1 catalyzed by electron transfer and their derivative curves (8×10^{-4} mol of $\mathbf{1}^+(PF_6^-)$ and 4.8×10^{-3} mol of $P(OMe)_3$ in 0.1 L of CH_3CN–0.1 M $Bu_4N^+BF_4^-$).

The chemical reaction investigated by our calorimetric method is the arene ligand replacement (1) in complexes (η_5-C_5H_5)-Fe^{II}(η^6-arene) ($\mathbf{1}^+$). This ligand exchange (1) can be performed

$$\underset{\mathbf{1}^+}{(\eta^5\text{-}C_5H_5)Fe^{II}(\eta^6\text{-}Ar)^+} + 3P(OMe)_3 \rightarrow \underset{\mathbf{2}^+}{(\eta^5\text{-}C_5H_5)Fe^{II}[P(OMe)_3]_3^+} + Ar \quad (1)$$

by heating,[7] but it slowly leads to low yield of $\mathbf{2}^+$. It is obvious that calorimetric studies are not possible in these experimental conditions. However, when reaction 1 is catalyzed[8a] by electron

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