ation occurs when two germaniums are directly bonded. In this case, extreme charge separation due to the small resonance integral becomes allowed.

This set of AM1 parameters illustrates a danger inherent to the flexibility of the semiempirical approach to quantum mechanics. Care must be taken in deriving parameters for the methods. Chemical knowledge and reasoned guidance are needed to develop parameters of chemical significance. The "human factor" is of paramount importance, as the best *mathematical* minima on the parameter hypersurface may not be the best *chemical* minima.[18]

In conclusion, caution should be exercised in calculations employing the AM1 germanium parameters when germanium atoms are bonded to one another. In this case, the tendency to localize charge is greatest. In combination with other elements, the germanium parameters appear to perform adequately. We *do not* recommend the replacement of the germanium β_p value. This would require a complete reparameterization for germanium, as the atomic parameters for an element are strongly interdependent (see above). It must be emphasized that setting $\beta_p = -2.500000$ was used for *trial* calculations, intended to illustrate that the magnitude of the AM1 value was too small.[19] It is NOT PROPOSED as a replacement for the default parameter. We in no way intend to encourage the manual alteration of parameters to achieve particular effects.

With elucidation of the current problem with the germanium parameters for AM1, it is apparent that this element should be reparameterized. With most elements, this is not an option because the developed values are used in subsequent parameterizations of other elements. This is not the case with germanium. Germanium data have not been used in any other molecular basis set for parameterization. While uncommon, silicon[20] and sulfur[21] were also reparameterized within the MNDO protocol due to poor performance. We do not wish to call for a general reparameterization, but in this single instance new work seems justified.

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(18) Parameterization schemes used for semiempirical methods generally rely on comparison of calculated values with a limited set of experimental data. Obviously, any such parameterization scheme is biased by the experimental data available or by the specific subset of molecules chosen for the basis set.

(19) The β_p value was altered to examine a specific feature of the performance of the germanium parameters and caused a number of other difficulties which were not listed. As an example, the heat of formation of 1 became over 165 kcal/mol more stable than the original parameters predicted.

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Electrophilic Thallation of Thiophene Derivatives and Furan with Phenylthallium(III) 18-Crown-6 Diperchlorate

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Summary: Electrophilic thallation of thiophene and its derivatives (2-methyl-, 2-chloro-, 2-bromo-, and 2-iodothiophenes, 2-thiopheneacetonitrile, 2-thiophenecarbonitrile, 3-methyl- and 3-bromothiophenes, and 3-thiophenecarboxaldehyde) as well as furan using (18-crown-6)phenylthallium(III) diperchlorate (**1**) (**1** is also named as phenylthallium(III) 18-crown-6 diperchlorate) was studied. The thallation occurred at the position α to the sulfur atom of thiophene and the oxygen atom of furan, affording the corresponding (18-crown-6)phenylarylthallium(III) perchlorate complexes **2**–**12**. The thallations of thiophenecarboxaldehydes took place without oxidation of the aldehyde groups.

In contrast to well-known aromatic thallation by inorganic Tl^{III} species, TlX_3, examples of electrophilic thallation by organothallium(III) compounds, e.g. $ArTlX_2$, have been limited.[1] The latter is interesting and important since it affords a mixed diarylthallium(III) compound that is a member of a relatively unknown class of organothallium compounds. Recently we have reported that a phenylthallium(III) complex having a crown ether, $[PhTl^{III}(18\text{-crown-}6)](ClO_4)_2$ (**1**), can initiate electrophilic thallation of phenols,[2] aromatic amines,[3] and pyrroles.[3] The presence of the crown ether is essential for a clean

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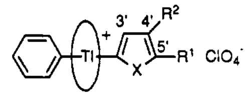
Table I. Yields of Reaction Products of Thiophenes and Furan



complex	X	R^1	R^2	yield/%
2	S	H	H	91
3		CH_3	H	63
4		Cl	H	84
5		Br	H	73
6		I	H	82
7		CH_2CN	H	43
8		CN	H	56^a
9		H	CH_3	92
10		H	Br	92
11		H	CHO	48
12	O	H	H	67

^{a} The reaction was carried out under reflux conditions.

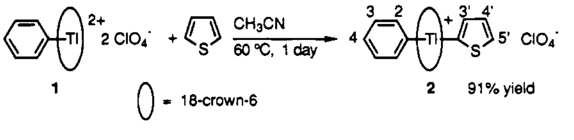
thallation, since the starting compounds $ArTlX_2$ (X = CF_3CO_2, ClO_4) are relatively thermally unstable. For example, disproportionation of phenylthallium(III) bis(trifluoroacetate) to diphenylthallium(III) trifluoroacetate occurred in acetone solution at reflux temperature.[4]

Described herein is a further exploitation of the new method applied to the thallation of thiophenes and furan. The results indicate that these heteroaromatics also undergo thallation featuring typical aromatic substitution and provide a series of new compounds that will be important in future structural study of organothallium compounds.

Results and Discussion

Electrophilic thallations of thiophenes and furan by $[PhTl^{III}(18\text{-crown-6})(ClO_4)_2$ (1) were investigated. In all cases studied the thallation readily proceeded only at the position α to the sulfur atom of thiophenes and the oxygen atom of furan, affording mixed diarylthallium(III) crown ether complexes in good to excellent yields. The ionic character of the Tl–C bonds in the products will also be discussed on the basis of the spin–spin coupling constants between the thallium nucleus and the protons in the phenyl group.

Reaction of 1 with Thiophenes and Furan. The electrophilic thallation of thiophene with 1 was carried out at 60 °C for 1 day to afford (18-crown-6)phenyl(2-thienyl)thallium(III) perchlorate (2) in 91% yield after recrystallization from CH_2Cl_2/Et_2O (eq 1).



(1)

1

2 91% yield

The thallated position in 2 was determined by the ^1H NMR spectrum. Assignment of the chemical shifts and the J_{TlH} values for H_2–H_4 and $H_{3'}$–$H_{5'}$ was done by examining the Tl–H spin–spin coupling patterns and utilizing the double-irradiation technique, as detailed in the previous paper.[3,6] In this compound one low-field signal and the two high-field signals for the protons in the thienyl group (δ 7.89, J_{TlH} = 165 Hz; δ 7.54, J_{TlH} = 255 Hz; δ 7.45, J_{TlH} = 78 Hz) were observed.[7] The assignment of the two β protons ($H_{3'}$ and $H_{4'}$) was made by comparison of the J_{TlH} values ($^3J_{TlH}$ = 255 and $^4J_{TlH}$ = 78 Hz, respectively) with those of thienylmercury compounds.[8]

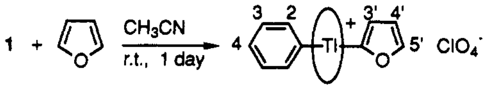
Table II. Selected J_{TlH} Values in 1–12

complex	J_{TlH_2}/Hz	$J_{TlH_{3'}}$/Hz	complex	J_{TlH_2}/Hz	$J_{TlH_{3'}}$/Hz
1	1173		7	540	270
2	529	255	8	536	267
3	521	275	9	522	255
4	544	288	10	547	244
5	546	284	11	544	258
6	545	274	12	527	200

The reaction of 1 with 4 equiv of thiophene in acetonitrile-d_3 at 60 °C was monitored by ^1H NMR spectroscopy for 24 h. The observed product was only 2, indicating the exclusive thallation at the position α to the sulfur atom.

The reactions of 1 with several substituted thiophenes were carried out, and the results are given in Table I. The thallated positions in the products, 3–11, were determined by the same procedure as described above. The thallations of 2-methyl-, 2-chloro-, 2-bromo-, and 2-iodothiophenes and 2-thiopheneacetonitrile gave the corresponding α-thallated complexes in good yields. A higher reaction temperature (reflux conditions) was required to accomplsih the thallation of 2-thiophenecarbonitrile. In the case of 3-methylthiophene, 3-bromothiophene, and 3-thiophenecarboxaldehyde, α-thallated compounds 9–11 were isolated in good to excellent yields.

The reaction of furan with 1 gave the α-thallated product, (18-crown-6)phenyl(2-furyl)thallium(III) perchlorate (12), in 67% yield under mild reaction conditions (room temperature) (eq 2).



(2)

12 67% yield

The fact that the CHO group remained intact in 11 may be related to the weak oxidizing ability of the thallium atom in 1, which was also observed in the reaction with catechol and pyrogallol.[2] It is also interesting to note that 1 reacted even with 2-thiophenecarbonitrile and 3-thiophenecarboxaldehydes having strong electron-withdrawing groups.

Ionic Character of the Tl–C Bonds. The selected spin–spin coupling constants between the thallium nucleus and the protons in phenyl and thienyl groups in 1–12 are listed in Table II.

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(4) McKillop et al. reported that arylthallium(III) bis(trifluoroacetate) compounds could be isolated as stable solids.[5] However, when an acetone solution of arylthallium(III) bis(trifluoroacetate) was refluxed, a disproportionation reaction of the compound occurred: Gun'kin, I. F.; Idelevich, A. I.; Butin, K. P. *Metalloorg. Khim.* **1990**, *3*, 602.

(5) McKillop, A.; Fowler, J. S.; Zelesko, M. J.; Hunt, J. D.; Taylor, E. C.; McGillivray, G. *Tetrahedron Lett.* **1969**, 2423.

(6) On strong irradiation of one component of each pair of the signals separated by J_{Tl}, the intensity of the other component of the pair decreases. Thus, this observation indicates that saturation transfer from the proton signal irradiated to the signals spin coupled with the thallium nucleus occurred. This saturation transfer method is useful for determination of each pair of the spin-separated proton signals.

(7) In general, the ^1H NMR resonances of the α protons in thiophenes will be observed at lower fields than those of β protons. For thiophenes and furans, see: (a) Gronowitz, S.; Hörnfelde, A. In *The Chemistry of Heterocyclic Compounds*; Taylor, E. C., Weissberger, A., Eds.; John Wiley & Sons: New York, 1991; pp 52–96. (b) Kellogg, R. M. In *Comprehensive Heterocyclic Chemistry*; Bird, C. W.; Cheeseman, G. W. H., Eds.; Pergamon Press: Oxford, U.K., 1984; pp 728–733. For metal-substituted thiophenes and furans see: (c) Bulman, M. J. *Tetrahedron* **1969**, *25*, 1443. (d) Lunazzi, L.; Tiecco, M.; Boicelli, C. A.; Taddei, F. *J. Mol. Spectrosc.* **1970**, *35*, 190. (e) Ebdon, A. P.; Huckerby, T. N.; Thorpe, F. G. *Tetrahedron Lett.* **1971**, 2921.

(8) These observations are in agreement with those in 2-thienylmercuric chloride. In 2-thienylmercuric chloride, the spin–spin coupling constants between the mercury nucleus and H_5 proton of the thienyl moiety were found to be larger than that between the mercury nucleus and H_4 proton.[7c–e]

The J_{TlH_2} values in 4–11 were slightly larger than those in 2 and 3. These J_{TlH_2} values in 2–12 are about 80 Hz larger than that in the pyrrole derivative, (18-crown-6)phenyl(2-pyrrolyl)thallium(III) perchlorate (13) (J_{TlH_2} = 449 Hz).[3] We have reported that J_{TlH_2} values give a criterion for the ionic character of the Tl–X bond trans to the phenyl group.[2,3,9,10] If we adopt this criterion in these complexes, the ionic character of the newly formed Tl–C bonds in 2–12 is larger than that in 13.[9] Somewhat larger ionic character of the Tl–C bonds in 2–12 as compared with that in 13 may be caused by larger electron-withdrawing abilities of the sulfur and the oxygen atoms than that of the nitrogen atom in the five-membered rings. We found that the ionic character in 2–12 is in the middle of that in (1,7-DTC)phenyl(phenylethynyl)thallium(III) perchlorate (J_{TlH_2} = 647 Hz)[11,12] and that in (18-crown-6)phenylmethylthallium(III) perchlorate (J_{TlH_2} = 402 Hz).[12]

Experimental Section

General Considerations. The ^{1}H NMR spectra were recorded on JEOL PS-100 and JEOL JNM-GSX27S spectrometers operating at 100 and 270 MHz, respectively. Chemical shifts of ^{1}H NMR signals are quoted relative to internal tetramethylsilane. Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet), coupling constant (Hz), relative intensity, and interpretation. IR spectra were measured on a Hitachi 215 or Hitachi 270-50 infrared spectrometer. Melting points were determined in open capillaries on a Mitamura Riken Kogyo melting point apparatus and are uncorrected.

Materials. (18-Crown-6)phenylthallium(III) diperchlorate (1) was synthesized by a published method.[2] Solvents except for acetonitrile were used without further purification. Acetonitrile was dried over P_2O_5 and purified by distillation under nitrogen atmosphere.

Caution! *Thallium compounds are highly toxic. The use of rubber gloves is strongly recommended for handling thallium compounds, whether inorganic or organic. Special care must also be taken in handling potentially explosive perchloric acid as well as perchlorate salts; chemists must prudently exercise safe practice in their manipulation and disposal.*

Preparation of (18-Crown-6)phenyl(2-thienyl)thallium(III) Perchlorate (2). In a typical preparation procedure, to a test tube containing 1 (0.745 g, 1.00 mmol) were added 2.5 mL of acetonitrile and thiophene (0.337 g, 4.00 mmol). This solution was degassed three times by freeze (liquid-nitrogen bath)–thaw (water bath) cycles, and then the tube was sealed under reduced pressure. The solution was heated at 60 °C for 24 h in the dark, and to the reaction mixture was added 100 mL of diethyl ether to enforce the precipitation of the product. The resulting solids were filtered out, and purification was carried out by addition of 100 mL of diethyl ether to a dichloromethane (5 mL) solution of the solids. The solids produced were filtered out and dissolved in 5 mL of acetonitrile. Addition of 100 mL of diethyl ether to the solution gave pure (18-crown-6)phenyl(2-thienyl)thallium(III) perchlorate (2), in 91% yield (0.663 g, 0.91 mmol), mp 271 °C dec. ^{1}H NMR (CD_3CN): δ 3.65 (s, 24 H, 18-crown-6), 7.67 (dd, J_{TlH} = 529 Hz, J_{HH} = 7.0 Hz, 2 H, H_2), 7.61 (dt, J_{TlH} = 173 Hz, J_{HH} = 7.0 Hz, 2 H, H_3), 7.46 (dt, J_{TlH} = 63 Hz, J_{HH} = 8.0 Hz, 1 H, H_4), 7.54 (dd, J_{TlH} = 255 Hz, J_{HH} = 2.0 Hz, 1 H, $H_{3'}$), 7.45 (dd, J_{TlH} = 78 Hz, J_{HH} = 5.0 Hz, 1 H, $H_{4'}$), 7.89 (dd, J_{TlH} = 165 Hz, J_{HH} = 5.0 Hz, 1 H, $H_{5'}$). IR (Nujol): ν(C–O–C and ClO_4) 1090 (s) cm^{-1}. Anal. Calcd for $C_{22}H_{32}ClO_{10}STl$: C, 36.28; H, 4.43. Found: C, 36.30; H, 4.39.

(18-Crown-6)phenyl(5-methyl-2-thienyl)thallium(III) perchlorate (3), mp 306 °C dec, was isolated in 63% yield (0.468 g, 0.63 mmol) after silica gel column chromatography (20 mm i.d. × 200 mm, eluent 1/2 CH_3CN/CH_2Cl_2, Wako gel C-200) and recrystallization from 5 mL/100 mL CH_2Cl_2/Et_2O. ^{1}H NMR (CD_3CN): δ 3.64 (s, 24 H, 18-crown-6), 7.66 (dd, J_{TlH} = 521 Hz, J_{HH} = 7.0 Hz, 2 H, H_2), 7.59 (dt, J_{TlH} = 173 Hz, J_{HH} = 7.0 Hz, 2 H, H_3), 7.45 (dt, J_{TlH} = 61 Hz, J_{HH} = 8.0 Hz, 1 H, H_4), 7.28 (d, J_{TlH} = 275 Hz, 1 H, $H_{3'}$), 7.28 (d, J_{TlH} = 98 Hz, 1 H, $H_{4'}$), 2.60 (d, J_{TlH} = 9 Hz, 3 H, CH_3). IR (Nujol): ν(C–O–C and ClO_4) 1090 (s) cm^{-1}. Anal. Calcd for $C_{23}H_{34}ClO_{10}STl$: C, 37.21; H, 4.62. Found: C, 37.71; H, 4.62.

(18-Crown-6)phenyl(5-chloro-2-thienyl)thallium(III) perchlorate (4), mp 195 °C dec, was isolated in 84% yield (0.64 g, 0.84 mmol) after recrystallization from 5 mL/100 mL CH_2Cl_2/Et_2O. ^{1}H NMR (CD_3CN): δ 3.66 (s, 24 H, 18-crown-6), 7.72 (dd, J_{TlH} = 544 Hz, J_{HH} = 7.0 Hz, 2 H, H_2), 7.63 (dt, J_{TlH} = 185 Hz, J_{HH} = 7.0 Hz, 2 H, H_3), 7.51 (dt, J_{TlH} = 72 Hz, J_{HH} = 8.0 Hz, 1 H, H_4), 7.63 (d, J_{TlH} = 288 Hz, 1 H, $H_{3'}$), 7.30 (d, J_{TlH} = 100 Hz, 1 H, $H_{4'}$). IR (Nujol): ν(C–O–C and ClO_4) 1086 (s) cm^{-1}. Anal. Calcd for $C_{22}H_{31}Cl_2O_{10}STl$: C, 34.64; H, 4.10. Found: C, 34.96; H, 4.20.

(18-Crown-6)phenyl(5-bromo-2-thienyl)thallium(III) perchlorate (5), mp 222 °C dec, was isolated in 73% yield (0.590 g, 0.73 mmol) after recrystallization from 5 mL/100 mL CH_2Cl_2/Et_2O. ^{1}H NMR (CD_3CN): δ 3.67 (s, 24 H, 18-crown-6), 7.72 (dd, J_{TlH} = 546 Hz, J_{HH} = 7.0 Hz, 2 H, H_2), 7.60 (dt, J_{TlH} = 184 Hz, J_{HH} = 7.0 Hz, 2 H, H_3), 7.48 (dt, J_{TlH} = 65 Hz, J_{HH} = 8.0 Hz, 1 H, H_4), 7.31 (d, J_{TlH} = 284 Hz, 1 H, $H_{3'}$), 7.43 (d, J_{TlH} = 96 Hz, 1 H, $H_{4'}$). IR (Nujol): ν(C–O–C and ClO_4) 1087 (s) cm^{-1}. Anal. Calcd for $C_{22}H_{31}BrClO_{10}STl$: C, 32.73; H, 3.87. Found: C, 32.99; H, 3.99.

(18-Crown-6)phenyl(5-iodo-2-thienyl)thallium(III) perchlorate (6), mp 268 °C dec, was isolated in 82% yield (0.700 g, 0.82 mmol) after recrystallization from 5 mL/100 mL CH_2Cl_2/Et_2O. ^{1}H NMR (CD_3CN): δ 3.65 (s, 24 H, 18-crown-6), 7.66 (dd, J_{TlH} = 545 Hz, J_{HH} = 7.0 Hz, 2 H, H_2), 7.61 (dt, J_{TlH} = 186 Hz, J_{HH} = 7.0 Hz, 2 H, H_3), 7.57 (dt, J_{TlH} = 61 Hz, J_{HH} = 8.0 Hz, 1 H, H_4), 7.22 (d, J_{TlH} = 274 Hz, 1 H, $H_{3'}$), 7.63 (d, J_{TlH} = 88 Hz, 1 H, $H_{4'}$). IR (Nujol): ν(C–O–C and ClO_4) 1089 (s) cm^{-1}. Anal. Calcd for $(C_{22}H_{31}ClIO_{10}STl)H_2O$: C, 30.29; H, 3.81. Found: C, 30.35; H, 3.63.

(18-Crown-6)phenyl(5-(cyanomethyl)-2-thienyl)thallium(III) perchlorate (7), mp 238 °C dec, was isolated in 43% yield (0.320 g, 0.43 mmol) after silica gel column chromatography (25 mm i.d. × 180 mm, eluent 1/5 CH_3CN/CH_2Cl_2, Wako gel C-200) and recrystallization from 5 mL/100 mL CH_2Cl_2/Et_2O. ^{1}H NMR (CD_3CN): δ 3.67 (s, 24 H, 18-crown-6), 7.70 (dd, J_{TlH} = 540 Hz, J_{HH} = 8.0 Hz, 2 H, H_2), 7.64 (dt, J_{TlH} = 177 Hz, J_{HH} = 7.0 Hz, 2 H, H_3), 7.44 (dt, J_{TlH} = 56 Hz, J_{HH} = 7.0 Hz, 1 H, H_4), 7.40 (dd, J_{TlH} = 270 Hz, J_{HH} = 4 Hz, 1 H, $H_{3'}$), 7.38 (d, J_{TlH} = 95 Hz, J_{HH} = 4 Hz, 1 H, $H_{4'}$), 4.14 (d, J_{HH} = 4 Hz, 2 H, CH_2CN). IR (Nujol): ν(CN) 2252 (w) cm^{-1}. Anal. Calcd for $C_{24}H_{33}ClNO_{10}STl$: C, 37.56; H, 4.33; N, 1.83. Found: C, 37.31; H, 4.33; N, 1.67.

Preparation of (18-Crown-6)phenyl(5-cyano-2-thienyl)thallium(III) Perchlorate (8). The reaction of 1 with 2-thiophenecarbonitrile was carried out in acetonitrile under refluxing condition for 24 h. The complex 8, mp 254 °C dec, was isolated in 56% yield (0.422 g, 0.56 mmol) after silica gel column chromatography (25 mm i.d. × 180 mm, eluent 1/5 CH_3CN/CH_2Cl_2, Wako gel FC-40) and recrystallization from 5 mL/100 mL CH_2Cl_2/Et_2O. ^{1}H NMR (CD_3CN): δ 3.67 (s, 24 H, 18-crown-6), 7.72 (dd, J_{TlH} = 536 Hz, J_{HH} = 7.0 Hz, 2 H, H_2), 7.62 (dt, J_{TlH} = 177 Hz, J_{HH} = 7.0 Hz, 2 H, H_3), 7.40 (dt, J_{TlH} = 64 Hz, J_{HH} = 8.0 Hz, 1 H, H_4), 7.38 (d, J_{TlH} = 267 Hz, 1 H, $H_{3'}$), 7.38 (d, J_{TlH} = 98 Hz, 1 H, $H_{4'}$). IR (Nujol): ν(CN) 2252 (w) cm^{-1}. Anal. Calcd for $C_{23}H_{31}ClNO_{10}STl$: C, 36.67; H, 4.15; N, 1.86. Found: C, 36.84; H, 4.16; N, 1.80.

(18-Crown-6)phenyl(4-methyl-2-thienyl)thallium(III) perchlorate (9), mp 234 °C dec, was isolated in 92% yield (0.683 g, 0.92 mmol) after recrystallization from 5 mL/100 mL CH_2Cl_2/Et_2O. ^{1}H NMR (CD_3CN): δ 3.65 (s, 24 H, 18-crown-6), 7.74 (dd, J_{TlH} = 522 Hz, J_{HH} = 7.0 Hz, 2 H, H_2), 7.60 (dt, J_{TlH} = 170 Hz, J_{HH} = 7.0 Hz, 2 H, H_3), 7.45 (dt, J_{TlH} = 63 Hz, J_{HH} = 8.0 Hz, 1 H, H_4), 7.27 (d, J_{TlH} = 255 Hz, 1 H, $H_{3'}$), 7.43 (d, J_{TlH} = 168 Hz, 1 H, $H_{5'}$), 2.36 (d, J_{TlH} = 26 Hz, 3 H, CH_3). IR (Nujol):

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(9) We have previously reported that the spin–spin coupling constants between the thallium nucleus and the protons, J_{TlH}, increase with increasing positive charge on the thallium atom.[2,3,10]

(10) Kawasaki, Y.; Enomoto, N.; Tomioka, J.; Akita, H. *J. Cood. Chem.* 1988, *18*, 157.

(11) 1,7-DTC is an abbreviation for 1,7-dithia-4,10,13,16-tetraoxacyclooctadecane.

(12) Unpublished result.

ν(C–O–C and ClO_4) 1089 (s) cm^{-1}. Anal. Calcd for $C_{23}H_{34}ClO_{10}STl$: C, 37.21; H, 4.62. Found: C, 37.45; H, 4.64.

(18-Crown-6)phenyl(4-bromo-2-thienyl)thallium(III) perchlorate (10), mp 223 °C dec, was isolated in 92% yield (0.743 g, 0.92 mmol) after recrystallization from 5 mL/100 mL CH_2Cl_2/Et_2O. ^{1}H NMR (CD_3CN): δ 3.62 (s, 24 H, 18-crown-6), 7.64 (dd, J_{TlH} = 547 Hz, J_{HH} = 7.0 Hz, 2 H, H_2), 7.56 (dt, J_{TlH} = 183 Hz, J_{HH} = 7.0 Hz, 2 H, H_3), 7.41 (dt, J_{TlH} = 66 Hz, J_{HH} = 8.0 Hz, 1 H, H_4), 7.34 (d, J_{TlH} = 244 Hz, 1 H, $H_{3'}$), 7.74 (d, J_{TlH} = 160 Hz, 1 H, $H_{5'}$). IR (Nujol): ν(C–O–C and ClO_4) 1086 (s) cm^{-1}. Anal. Calcd for $C_{22}H_{31}BrClO_{10}STl$: C, 32.73; H, 3.87. Found: C, 32.58; H, 3.99.

(18-Crown-6)phenyl(4-formyl-2-thienyl)thallium(III) perchlorate (11), mp 295 °C dec, was isolated in 48% yield (0.363 g, 0.48 mmol) after silica gel column chromatogaphy (20 mm i.d. × 150 mm, eluent 1/2 CH_3CN/CH_2Cl_2, Nakarai Tesque mesh 70–230) and recrystallization from 5 mL/100 mL CH_2Cl_2/Et_2O. ^{1}H NMR (CD_3CN): δ 3.64 (s, 24 H, 18-crown-6), 7.70 (dd, J_{TlH} = 544 Hz, J_{HH} = 7.0 Hz, 2 H, H_2), 7.59 (dt, J_{TlH} = 182 Hz, J_{TlH} = 7.0 Hz, 2 H, H_3), 7.45 (dt, J_{TlH} = 65 Hz, J_{HH} = 8.0 Hz, 1 H, H_4), 7.79 (d, J_{TlH} = 258 Hz, 1 H, $H_{3'}$), 8.65 (d, J_{TlH} = 157 Hz, 1 H, $H_{5'}$), 10.20 (d, J_{TlH} = 66 Hz, 1 H, CHO). IR (Nujol): ν(C=O) 1680 (s) cm^{-1}. Anal. Calcd for $C_{23}H_{32}ClO_{11}STl$: C, 36.52; H, 4.26. Found: C, 36.24; H, 4.18.

Preparation of (18-Crown-6)phenyl(2-furyl)thallium(III) Perchlorate (12). The reaction of 1 (0.745 g, 1.00 mmol) with furan (0.272 g, 8.00 mmol) was carried out at room temperature for 1 day. The complex 13 (0.477 g, 67%), mp >230 °C dec, was isolated after recrystallization from 5 mL/100 mL CH_2Cl_2/Et_2O. ^{1}H NMR (CD_3CN): δ 3.67 (s, 24 H, 18-crown-6), 7.69 (dd, J_{TlH} = 527 Hz, J_{HH} = 7.0 Hz, 2 H, H_2), 7.66 (dt, J_{TlH} = 170 Hz, J_{HH} = 7.0 Hz, 2 H, H_3), 7.42 (dt, J_{TlH} = 64 Hz, J_{HH} = 8.0 Hz, 1 H, H_4), 7.37 (d, J_{TlH} = 200 Hz, 1 H, $H_{3'}$), 6.90 (d, J_{TlH} = 62 Hz, 1 H, $H_{4'}$), 7.31 (d, J_{TlH} = 38 Hz, 1 H, $H_{5'}$). IR (Nujol): ν(C–O–C and ClO_4) 1080 (s) cm^{-1}. Anal. Calcd for $C_{22}H_{32}ClO_{11}Tl$: C, 37.10; H, 4.53. Found: C, 37.04; H, 4.59.

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Kinetic and Chemical Evidence for the Participation of Mononuclear Catalytic Species in the Homogeneous Hydrogenation of Diphenylacetylene Promoted by an Edge-Bridged Triruthenium Carbonyl Cluster Complex

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Summary: The edge-bridged cluster complex $[Ru_3(\mu\text{-}H)(\mu\text{-}C_8H_{11}N_2)(CO)_9]$ (**1**) ($C_8H_{12}N_2$ = 1,2-diamino-4,5-dimethylbenzene) is a catalyst precursor for the selective homogeneous hydrogenation of diphenylacetylene to stilbene under very mild conditions. The binuclear ruthenium(I) alkenyl derivative $[Ru_2(\mu\text{-}C_8H_{11}N_2)(\mu\text{-}\eta^1,\eta^2\text{-}PhC{=}C(H)Ph)(CO)_5]$ (**2**), which has been observed during the catalytic reaction, has been isolated from the reaction of **1** with diphenylacetylene; however, **2** does not react with hydrogen. These results, coupled to a kinetic study of the catalytic reaction, which follows the rate law $-d[H_2]/dt = K[\mathbf{1}](P(H_2))$, where $K = 9.18 \times 10^{-3}$ atm^{-2} s^{-1} at 333 K, suggest that the catalytic species is mononuclear.

Introduction

There is great interest in the search for bi- or polynuclear complexes in which two or more metal centers are active in catalysis under homogeneous conditions.[1] However, this has been confirmed only in a few instances.[1a] In other cases, it is known that the original polynuclear framework fragments to give species of different nuclearity,[2] but in most cases, the fate of the catalytic precursor is unknown.[1] The use of ligand-bridged polynuclear complexes has been claimed as a method for preventing cluster degradation,[3] but it has met only a limited success.[4] In this context, the knowledge of the reaction kinetics is essential to establish the nuclearity of the catalytic species and the reaction mechanisms.[1a]

We have been interested in the effectiveness of ligand-bridged triruthenium cluster complexes as homogeneous catalyst precursors in hydrogenation reactions.[5,6] Here we report the reactivity of diphenylacetylene and hydrogen with $[Ru_3(\mu\text{-}H)(\mu\text{-}C_8H_{11}N_2)(CO)_9]$ (1) ($C_8H_{12}N_2$ = 1,2-diamino-4,5-dimethylbenzene), a cluster complex containing an edge-bridging N-donor ligand,[7] and its use as catalyst

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