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Electrophilic Thallation of Aniline Derivatives and Nitrogen Heterocycles with Phenylthallium(III) 18-Crown-6 Diperchlorate

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Electrophilic thallation of diphenylamine, diphenylmethylamine, triphenylamine, pyrrole, *N*-methylpyrrole, and pyrazole with $[PhTl^{III}(18\text{-crown-}6)](ClO_4)_2$ (1) gives compounds of the type $[PhArTl^{III}(18\text{-crown-}6)](ClO_4)$ (Ar = aryl = 4′-(phenylamino)phenyl, 4′-(methylphenylamino)phenyl, 4′-(diphenylamino)phenyl, 2′-pyrrolyl, 2′-*N*-methylpyrrolyl, and 4′-pyrazolyl, respectively). On the other hand, the reaction of 1 with imidazole resulted in coordination of imidazole nitrogen to the thallium ion without substitution at the ring. The character of Tl–C bonds formed by the thallation is discussed on the basis of spin–spin coupling constants between thallium nucleus and ortho protons of the phenyl group, $^3J_{TlH_2}$.

Introduction

Electrophilic aromatic substitution reactions have been widely investigated. Electron-rich aromatic compounds such as aromatic amines[1] and five-membered heterocycles[2] tend to undergo polysubstitution. For example, halogenation reactions of aniline and pyrrole afford trihalogenated aniline and tetrahalogenated pyrrole, respectively. Polymercuration[3] of aromatic amines and five-membered nitrogen heterocycles such as aniline,[3b] pyrrole,[3c,d] and indole[3e] also occurred by the use of HgX_2 (X = OAc, NCO), which are the only examples of metalation of nitrogen-containing aromatic derivatives. On the other hand, the reaction of $HgCl_2$ with aniline[4] and pyrrole[5] afforded no mercuration products but Hg–N bonded compounds.

We previously reported the electrophilic thallation of several phenols using (18-crown-6)(phenyl)thallium(III) diperchlorate (1; also called phenylthallium(III) 18-crown-6 diperchlorate).[6,7] In these reactions, the thallation occurred exclusively at the position para to electron-donating group such as OH and OCH_3 and no polythallated product was observed. This result may be traced to steric and/or electronic origins. The electronic origin of the exclusive monothallation may be attributed to electronic repulsion between the positive charge induced at the aromatic ring of the monothallation product and the second molecule of 1. On the basis of this consideration, it was interesting to examine if monothallation predominates even for more electron-rich compounds such as aromatic amines and nitrogen heterocycles. The results, which are the subject of this paper, indicate clean monothallation and provide a simple method for the synthesis of unsymmetrical diarylthallium(III) complexes. The character of the Tl–C bonds of the new compounds obtained will be also discussed on the basis of spin–spin coupling constants between thallium nucleus and ortho protons of the phenyl group, $^3J_{TlH_2}$.

Table I. Selected Spectral Data (J_{TlH}, Hz)

complex[a]	J_{TlH_2}	$J_{TlH_2'}$	$J_{TlH_3'}$
2	440	435	117
3	444	429	114
4	440	425	112
5	449		212
6	450		217
7	562		104
8	953	41	
9	903		

Results and Discussion

The reactions of the $[PhTl^{III}(18\text{-crown-}6)](ClO_4)_2$ (1) with phenylamine derivatives such as aniline, diphenylamine, diphenylmethylamine, and triphenylamine were studied. The reactions of 1 with some nitrogen heterocycles such as pyrrole, *N*-methylpyrrole, pyrazole, imidazole, and *N*-methylimidazole were also examined. All the reactions gave products having a Tl–C bond as the result of aromatic substitution, except for the case of imidazole derivatives which resulted in straightforward coordination on the thallium ion. The reaction with aniline was another exception (vide infra).

Although extensive studies of the reactions of inorganic Tl^{III}, i.e. $Tl(NO_3)_3$, with a variety of aromatic compounds have been reported,[8] the reaction of Tl^{III} with nitrogen

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[5] (a) Fischer, H.; Muller, R. *Hoppe-Seyler's Z. Physiol. Chem.* **1925**, *148*, 155. (b) Willstatter, R.; Asahina, Y. *Liebigs Ann. Chem.* **1911**, *385*, 195.

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[7] Complex 1 is isolated as a monohydrate.

[8] (a) Usyatinskii, A. Ya.; Bregadze, V. I. *Usp. Khim.* **1988**, *57*, 1840; Usyatinskii, A. Ya.; Bregadze, V. I. *Russ. Chem. Rev. (Engl. Transl.)* **1988**, *57*, 1054 and references cited therein. (b) Uemura, S. In *Synthetic Reagents*; Pizey, J. S., Ed.; Ellis Horwood: New York, 1983; Vol. 5, Chapter 3. (c) McKillop, A.; Taylor, E. C. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 7, Chapter 47. (d) McKillop, A.; Taylor, E. C. *Adv. Organomet. Chem.* **1973**, *11*, 147 and references cited therein.

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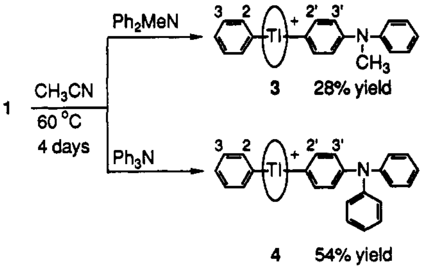
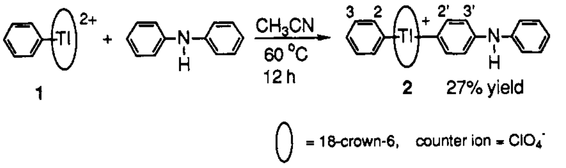
Scheme I



aromatics leading to isolable products having Tl–C bonds has not been reported, to the best of our knowledge.

Reaction of $[PhTl^{III}(18\text{-crown-}6)](ClO_4)_2$ (1) with Aniline and Its Derivatives. The reactions of 1 with diphenylamine was carried out in acetonitrile at 60 °C for 12 h to give (18-crown-6)(phenyl)[4′-(phenylamino)phenyl]thallium(III) perchlorate (**2**) in 27% yield (eq 1).

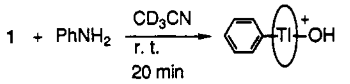


(1)

In the ^1H NMR spectrum of **2**, the resonances of one phenyl ring ($H_{2'}$ and $H_{3'}$) of the diphenylamino group exhibited spin–spin coupling with the thallium nucleus (see Table I), and the proton resonances of the other phenyl ring were observed as multiplets at δ 6.6–7.5 without spin–spin coupling with thallium nucleus. Chemical shifts of H_2, H_3, $H_{2'}$, and $H_{3'}$ were assigned by the following procedure. Signals of H_2 and $H_{2'}$ were observed as a doublet of doublets, and the H_3 and $H_{3'}$ signals could be distinguished by the spectral pattern (H_3, doublet of triplets; $H_{3'}$, doublet of doublets). In order to assign the H_2 and $H_{2'}$, strong irradiation of either higher field or lower field component of the H_3 triplet pair proton separated by J_{Tl} was performed. This irradiation resulted in, besides disappearance of the other component of the H_3 pair, collapse of the corresponding component of the H_2 doublet pair into a singlet. An N–H stretching frequency, ν(N–H), was observed at 3364 cm^{-1} in the solid state by IR spectroscopy. These results suggest that the thallation occurred only on one phenyl group at the position para to the amino group. The ^1H NMR spectra of a reaction mixture between 1 and diphenylamine in CD_3CN showed almost exclusive formation of **2**, without any multithallation product having been detected within an accuracy of the ^1H NMR spectral measurement.

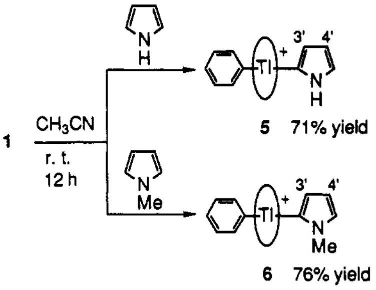
Analogous reactions with diphenylmethylamine and triphenylamine also led to thallation on only one phenyl group and at the position para to the amino group (Scheme I). The thallated positions in the products were determined by the same procedure as that described above. The products, (18-crown-6)(phenyl)[4′-(methylphenylamino)phenyl]thallium(III) perchlorate (**3**) and (18-crown-6)(phenyl)[4′-(diphenylamino)phenyl]thallium(III) perchlorate (**4**), were isolated in 28% and 54% yields, respectively, after silica gel column chromatography and recrystallization from CH_2Cl_2/Et_2O or CH_3CN/Et_2O.

Contrary to these, aniline did not undergo thallation with 1 but gave only $[Ph(OH)Tl^{III}(18\text{-crown-}6)](ClO_4)$[9a] at room temperature (eq 2). This compound may have been formed by deprotonation from H_2O coordinated to thallium atom in 1.[7]

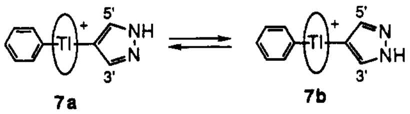


(2)

Scheme II

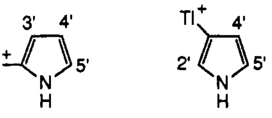


Scheme III



7a **7b**

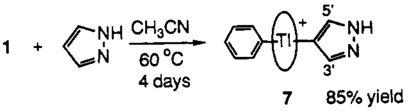
Chart I



A B

Reaction of 1 with Five-Membered Nitrogen Heterocycles. The thallation of pyrrole with 1 in acetonitrile at room temperature for 12 h occurred only at the α-position to give (18-crown-6)(phenyl)(2′-pyrrolyl)thallium(III) perchlorate (**5**) in 71% isolated yield (Scheme II). Determination of the thallated position in **5** was made by the values of the spin–spin coupling constant between the thallium nucleus and pyrrolyl group protons. Assignment of the pyrrolyl proton resonances and determination of the coupling constants were made by strong irradiation of one component of each pair separated by J_{Tl}, resulting in a significant decrease in intensity of the other component. When thallation occurs at the α-position (See A of Chart I), three resonances of the pyrrolyl group ($H_{3'}$, $H_{4'}$, $H_{5'}$) with $^3J_{Tl}$(Tl–C–C–H), $^4J_{Tl}$(Tl–C–C–C–H), and $^4J_{Tl}$(Tl–C–N–C–H), respectively, would be observed: i.e. one large and two small spin–spin coupling constants. In the case of thallation at the β-position (B), three resonances of the pyrrolyl group ($H_{2'}$, $H_{4'}$, $H_{5'}$) with $^3J_{Tl}$(Tl–C–C–H), $^3J_{Tl}$(Tl–C–C–H), and $^4J_{Tl}$(Tl–C–C–C–H), respectively, would be observed: i.e. two large and one small spin–spin coupling constant. The spin–spin coupling constants observed in **5** are 212, 76, and 55 Hz. One large and two small J values suggest that the thallium moiety is located at the α-position (A). Formation of multiply thallated complexes were not detected in the reaction mixture, even if a 4-fold excess of 1 was used. The thallation of N-methylpyrrole also took place at the α-position, and the complex was isolated in 76% yield (Scheme II).

The thallation of pyrazole took place at the 4-position to give (18-crown-6)(phenyl)(4′-pyrazolyl)thallium(III) perchlorate (**7**) in 85% isolated yield (eq 3). An IR absorption at 3108 cm^{-1} indicated the presence of an N–H



(3)

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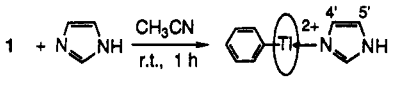
bond in 7. In the ^{1}H NMR spectrum of 7, only one kind of C–H signal of the pyrazole moiety was observed. This result suggests that there is a rapid movement of the N–H hydrogen as shown in Scheme III.

Reaction of 1 with Imidazole and *N*-Methylimidazole. The reaction with imidazole was carried out at room temperature for 1 h. Colorless solids were obtained by addition of diethyl ether to the reaction mixture. The elemental analysis of the product agrees with the formula (18-crown-6)(imidazole)(phenyl)thallium(III) diperchlorate (8), and the isolated yield of the adduct was 89% after recrystallization from CH_3CN/Et_2O (eq 4). In an IR measurement in Nujol mull, the ν(N–H) band was observed at 3160 cm^{-1}. The ^{1}H NMR spectrum of 8 showed ${}^{3}J_{\mathrm{TlH_2}}$ = 953 Hz for ortho protons of the phenyl group, which is much larger than those of 2–7 (see Table I) but only slightly smaller than that of 1 (1173 Hz).[6,9] In light of our previous results,[6,9] these observations suggest only a small reduction of effective positive charge on the thallium atom in 8 as compared to that in 1, and the coordination of imidazole in 8 through its sp^2 nitrogen atom is deduced. Bonding to the thallium ion with the other nitrogen (i.e., N_1) is unfavorable since the aromaticity of the ring is thereby lost.[10]

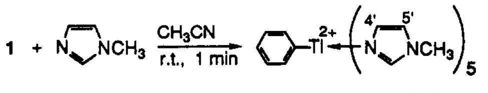


(4)

8 89% yield

Reactions of 8 with NaCl and triethylamine were carried out in CD_3CN/D_2O and CD_3CN, respectively, at room temperature. In the former reaction, the imidazole ligand was substituted with chloride ion, giving [Ph(Cl)Tl$^{\mathrm{III}}$(18-crown-6)](ClO_4).[11] In the latter, however, the product was [Ph(OH)Tl$^{\mathrm{III}}$(18-crown-6)](ClO_4),[9a] which may be formed by a reaction of 1 with OH$^-$ which was generated by triethylamine and moisture in CD_3CN. The coordinated imidazole, however, was not substituted with pyridine even after heating at 60 °C for 1 day in acetonitrile containing a large excess of pyridine. The steric bulk of imidazole and 18-crown-6 would have prohibited the approach of a large ligand such as pyridine. We cannot rule out the alternative possibility that the substitution reaction by pyridine is thermodynamically unfavored. However, the reaction of 1 with pyridine afforded only [Ph(OH)Tl$^{\mathrm{III}}$(18-crown-6)](ClO_4), which is produced by a deprotonation reaction from 1.

When the reaction of 1 with 10 equiv of *N*-methylimidazole[12] was carried out at room temperature, colorless precipitates appeared immediately. In contrast to the reaction with imidazole, the complex obtained was found to be crown ether free pentakis(*N*-methylimidazole)(phenyl)thallium(III) diperchlorate (9) (90% isolated yield) (eq 5) on the basis of an elemental analysis. This complex may be produced by coordination of *N*-methylimidazole to the phenylthallium(III) ion which was generated by dissociation of 18-crown-6 from 1. It is uncertain why the reaction of 1 with imidazole gives adduct 8 and the reaction of 1 with *N*-methylimidazole gives the crown ether free comlex 9.



(5)

9 90% yield

Ionic Character of the Tl–X Bonds (X = C, N). Selected J_{TlH} values for complexes 2–9 are given in Table I. Spin–spin coupling constants between the thallium nucleus and phenyl group protons, ${}^{3}J_{\mathrm{TlH_2}}$ and ${}^{4}J_{\mathrm{TlH_3}}$, in [Ph(X)Tl$^{\mathrm{III}}$(18-crown-6)]$(ClO_4)_n$ (n = 1, 2) reflect the ionic character of the Tl–X bonds: I.e., they increase with increasing effective positive charge on thallium atom.[6,9]

In complexes 2–4, the values of ${}^{3}J_{\mathrm{TlH_2}}$ are in a range of 440–450 Hz. These values are larger than the values of [Ph(CH_3)Tl$^{\mathrm{III}}$(18-crown-6)](ClO_4) (10) (402 Hz)[13] and are comparable with those of [Ph(4′-HOC_6H_4)Tl$^{\mathrm{III}}$(18-crown-6)](ClO_4) (11) (447 Hz)[6] and [Ph(4′-$MeOC_6H_4$)Tl$^{\mathrm{III}}$(18-crown-6)](ClO_4) (12) (454 Hz).[13] It is suggested from these results that electronic factors of the substituent at the 4′-position of the C_6H_4X group (X = NR^1R^2, OH, OMe) and of the substituents on the nitrogen atom (NR^1R^2: R^1 = H, R^2 = Ph; R^1 = Me, R^2 = Ph; R^1 = R^2 = Ph) do not greatly affect the Tl–C bond character.

The values of ${}^{3}J_{\mathrm{TlH_2}}$ in 5 and 6 are also observed to be about 450 Hz, suggesting that the ionic character of Tl–C bonds is similar to those of Tl–C bonds in 2–4, 11, and 12. The substituent on the nitrogen atom in 5 and 6 (H and Me, respectively) causes no appreciable effect on the Tl–C bonds.

The value of ${}^{3}J_{\mathrm{TlH_2}}$ in 7 is about 110 Hz larger than that in 5. This may be due to the increase of ionic character of the Tl–C bond, as a result of an electron-withdrawing ability of the additional nitrogen atom.

It is interesting that in 8 containing the Tl–N bond spin–spin couplings between the thallium nucleus and the imidazole protons through the Tl–N bond (41, 52, 41 Hz) were observed. This observation indicates that the Tl–N bond in 8 has somewhat covalent bond character, which is consistent with the inertness of this complex to the ligand-exchange reaction with pyridine.

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, m = multiplet), coupling constant (Hz), relative intensity, and interpretation. IR spectra were measured on a Hitachi 215 or a 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)(phenyl)thallium(III) diperchlorate was synthesized by published method.[6] Aniline, pyrrole, and *N*-methylpyrrole were purified by distillation under nitrogen atmosphere. Diphenylamine and triphenylamine were purified by recrystallization. Triethylamine and pyridine were dried over CaH_2 and purified by distillation under nitrogen atmosphere. 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; manipulations employing screening

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[10] (a) Reedijk, J. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, 1987; Vol. 2, pp 73–98. (b) Sundberg, R. J.; Martin, R. B. *Chem. Rev.* **1974**, *74*, 471.

[11] Unpublished result. The values of spin–spin coupling constants between the thallium nucleus and phenyl protons in [Ph(Cl)Tl$^{\mathrm{III}}$(18-crown-6)](ClO_4) were 930 ($J_{\mathrm{TlH_2}}$), 359 ($J_{\mathrm{TlH_3}}$), and 122 Hz ($J_{\mathrm{TlH_4}}$). These values agreed with those of the product obtained by the reaction of 1 with sodium chloride.

[12] When the reaction of 1 with 4 equiv of *N*-methylimidazole was carried out under the same conditions as in the NMR tube, complexes 1 and 9 were observed.

[13] Unpublished results.

of the apparatus are strongly advised.

Preparation of (18-Crown-6)(phenyl)[4′-(phenylamino)phenyl]thallium(III) Perchlorate (2). To a test tube containing (18-crown-6)(phenyl)thallium(III) diperchlorate (1) (0.372 g, 0.50 mmol) were added 5 mL of acetonitrile and diphenylamine (0.338 g, 2.0 mmol). The solution was degassed three times by freeze (liquid nitrogen bath)–thaw (water bath) cycles, and the tube was sealed under reduced pressure. The reaction mixture was heated at 60 °C for 12 h in the darkness, and to this solution was added 100 mL of diethyl ether. Oils produced were decanted and purified by silica gel column chromatography (eluent $CH_3CN/CH_2Cl_2 = 2/1$, 20-mm i.d. × 250-mm length, Nakarai Tesque mesh 70–230) to give light purple solids. These were purified by dissolution in acetonitrile (5 mL), followed by addition of 100 mL of diethyl ether to afford **2** as light purple solids, in 27% yield (0.110 g, 0.14 mmol): mp >260 °C dec; ^1H NMR (CD_3CN) 3.63 (s, 24 H, 18-crown-6), 6.6–7.5 (m, 5 H, NC_6H_5), 7.78 (dd, J_{TlH} = 440 Hz, J_{HH} = 7.0 Hz, 2 H, H_2), 7.60 (dd, J_{TlH} = 435 Hz, J_{HH} = 8.0 Hz, 2 H, $H_{2'}$), 7.33 (dd, J_{TlH} = 117 Hz, J_{HH} = 8.0 Hz, 2 H, $H_{3'}$) (chemical shifts of H_3, H_4, and NH resonances could not be determined because these signals overlapped with other signals); IR (Nujol) ν(N–H) 3364 (m) cm^{-1}. Anal. Calcd for $(C_{30}H_{39}ClNO_{10}Tl)_2H_2O$: C, 43.81; H, 4.90; N, 1.70. Found: C, 43.65; H, 4.89; N, 1.73.

Preparation of (18-Crown-6)(phenyl)[4′-(methylphenylamino)phenyl]thallium(III) Perchlorate (3). In a 20-mL round-bottomed flask was placed **1** (0.372 g, 0.5 mmol), and the flask was charged with nitrogen. To this were added 5 mL of acetonitrile and diphenylmethylamine (0.367 g, 2.0 mmol). This solution was heated at 60 °C for 4 days. The reaction mixture was transferred to 100-mL flask. To the reaction mixture was added 100 mL of diethyl ether to give purple oils. These oils were purified by silica gel column chromatography (eluent $CH_3CN/CH_2Cl_2 = 1/5$, 20-mm i.d. × 250-mm length, Nakarai Tesque mesh 70–230). Light purple solids obtained were dissolved in dichloromethane (10 mL). Addition of 100 mL of diethyl ether to this afforded pure **3**, as light purple solids in 28% yield (0.116 g, 0.14 mmol): mp 239 °C dec; ^1H NMR (CD_3CN) 3.38 (s, 3 H, CH_3), 3.60 (s, 24 H, 18-crown-6), 7.1–7.2 (m, 5 H, NC_6H_5), 7.77 (dd, J_{TlH} = 444 Hz, J_{HH} = 7.0 Hz, 2 H, H_2), 7.57 (dt, J_{TlH} = 140 Hz, J_{HH} = 8.0 Hz, 2 H, H_3), 7.52 (dd, J_{TlH} = 429 Hz, J_{HH} = 8.0 Hz, 2 H, $H_{2'}$), 7.02 (dd, J_{TlH} = 114 Hz, J_{HH} = 8.0 Hz, 2 H, $H_{3'}$) (chemical shift of the H_4 resonance could not be determined because it overlapped with other signals); IR (Nujol) ν(C–O–C and ClO_4) 1084 (s) cm^{-1}. Anal. Calcd for $C_{31}H_{41}ClNO_{10}Tl$: C, 45.00; H, 4.99; N, 1.69. Found: C, 44.60; H, 5.02; N, 1.64.

Preparation of (18-Crown-6)(phenyl)[4′-(diphenylamino)phenyl]thallium(III) Perchlorate (4). An acetonitrile (20 mL) solution of **1** (0.745 g, 1.0 mmol) and triphenylamine (0.981 g, 4.0 mmol) was heated at 60 °C for 4 days under nitrogen atomsphere. To the reaction mixture was added 200 mL of diethyl ether. Dark green oils obtained were dissolved in dichloromethane (50 mL), and this solution of oils was washed with two 50-mL portions of deionized water. The dichloromethane layer was dried over $MgSO_4$ and evaporated in vacuo at room temperature to give green solids. Addition of 100 mL of diethyl ether to an acetonitrile (10 mL) solution of the solids afforded pure **4** as green solids in 54% yield (0.481 g, 0.54 mmol): mp >285 °C dec; ^1H NMR (CD_3CN) 3.69 (s, 24 H, 18-crown-6), 7.0–7.5 (m, 10 H, $N(C_6H_5)_2$), 7.67 (dd, J_{TlH} = 440 Hz, J_{HH} = 7.0 Hz, 2 H, H_2), 7.54 (dt, J_{TlH} = 142 Hz, J_{HH} = 7.0 Hz, 2 H, H_3), 7.44 (dd, J_{TlH} = 425 Hz, J_{HH} = 8.0 Hz, 2 H, $H_{2'}$), 7.12 (dd, J_{TlH} = 112 Hz, J_{HH} = 8.0 Hz, 2 H, $H_{3'}$) (chemical shift of the H_4 resonance could not be determined because it overlapped with other signals); IR (Nujol) ν(C–O–C and ClO_4) 1084 (s) cm^{-1}. Anal. Calcd for $(C_{36}H_{43}ClNO_{10}Tl)_2CH_3CN$: C, 48.83; H, 4.93; N, 2.31. Found: C, 48.95; H, 5.04; N, 2.45.

Preparation of (18-Crown-6)(phenyl)(2′-pyrrolyl)thallium(III) Perchlorate (5). A 20-mL round-bottomed flask containing **1** (1.489 g, 2.0 mmol) was charged with nitrogen. To this were added 5 mL of acetonitrile and pyrrole (0.537 g, 8.0 mmol). After the mixture was stirred at room temperature for 12 h, colorless solids precipitated. The solids were filtered with suction (A). An additional amount of brown solids was obtained by addition of 100 mL of diethyl ether to the filtrate. A dichloromethane (30-mL) solution of the brown solids was washed with two 50-mL portions of deionized water, dried over $MgSO_4$, and concentrated under reduced pressure at room temperature. Addition of 100 mL of diethyl ether to the concentrated solution afforded colorless solids (B). Both A and B are pure **5** (71% yield, 1.00 g, 1.42 mmol): mp 312 °C dec; ^1H NMR (CD_3CN) 3.64 (s, 24 H, 18-crown-6), 7.71 (dd, J_{TlH} = 449 Hz, J_{HH} = 7.0 Hz, 2 H, H_2), 7.57 (dt, J_{TlH} = 141 Hz, J_{HH} = 7.0 Hz, 2 H, H_3), 7.42 (dt, J_{TlH} = 67 Hz, J_{HH} = 8.0 Hz, 1 H, H_4), 6.62 (d, J_{TlH} = 212 Hz, 1 H, $H_{3'}$), 6.80 (d, J_{TlH} = 76 Hz, 1 H, $H_{4'}$), 6.71 (d, J_{TlH} = 55 Hz, 1 H, $H_{5'}$); IR (Nujol) ν (N–H) 3352 (m) cm^{-1}. Anal. Calcd for $C_{22}H_{33}ClNO_{10}Tl$: C, 37.15; H, 4.68; N, 1.97. Found: C, 37.12; H, 4.69; N, 1.96.

Preparation of (18-Crown-6)(phenyl)(2′-*N*-methylpyrrolyl)thallium(III) Perchlorate (6). Reactants (**1**, 0.372 g, 0.50 mmol; *N*-methylpyrrole, 0.162 g, 2.0 mmol) were dissolved in 5 mL of acetonitrile in a 20-mL round-bottomed flask. This solution was stirred at room temperature under nitrogen atmosphere in the darkness for 12 h. To the reaction mixture was added 100 mL of diethyl ether. Pale yellow solids that precipitated were dissolved in 50 mL of dichloromethane, and the resulting solution was washed with four 50-mL portions of deionized water. The organic layer was dried over $MgSO_4$ and evaporated in vacuo at room temperature to give colorless solids. Addition of 100 mL of diethyl ether to a dichloromethane (5 mL) solution of the solids afforded **6** as colorless solids in 76% yield (0.273 g, 0.38 mmol): mp >260 °C dec; ^1H NMR (CD_3CN) 3.69 (s, 24 H, 18-crown-6), 7.76 (dd, J_{TlH} = 450 Hz, J_{HH} = 7.0 Hz, 2 H, H_2), 7.61 (dt, J_{TlH} = 146 Hz, J_{HH} = 8.0 Hz, 2 H, H_3), 7.38 (dt, J_{TlH} = 60 Hz, J_{HH} = 8.0 Hz, 1 H, H_4), 3.79 (d, J_{TlH} = 6 Hz, 3 H, CH_3), 6.56 (d, J_{TlH} = 217 Hz, 1 H, $H_{3'}$), 6.72 (d, J_{TlH} = 94 Hz, 1 H, $H_{4'}$), 7.20 (d, J_{TlH} = 65 Hz, 1 H, $H_{5'}$); IR (Nujol) ν(C–O–C and ClO_4) 1095 (s) cm^{-1}. Anal. Calcd for $C_{23}H_{35}ClNO_{10}Tl$: C, 38.09; H, 4.86; N, 1.93. Found: C, 37.70; H, 4.92; N, 2.33.

Preparation of (18-Crown-6)(phenyl)(4′-pyrazolyl)thallium(III) Perchlorate (7). Reactants (**1**, 0.372 g, 0.50 mmol; pyrazole, 0.136 g, 2.00 mmol) were dissolved in 5 mL of acetonitrile in a test tube. The solution was degassed three times by freeze (liquid nitrogen bath)–thaw (water bath) cycles, and then the tube was sealed under reduced pressure. This solution was heated at 60 °C for 4 days in the darkness. To the reaction mixture was added 100 mL of diethyl ether to give colorless precipitates. Addition of 100 mL of diethyl ether to a dichloromethane (5 mL) solution of the solids afforded **7** as colorless solids in 85% yield (0.303 g, 0.43 mmol): mp 225 °C dec; ^1H NMR (CD_3CN) 3.66 (s, 24 H, 18-crown-6), 7.75 (dd, J_{TlH} = 562 Hz, J_{HH} = 7.0 Hz, 2 H, H_2), 7.65 (dt, J_{TlH} = 187 Hz, J_{HH} = 7.0 Hz, 2 H, H_3), 7.57 (dt, J_{TlH} = 65 Hz, J_{HH} = 8.0 Hz, 1 H, H_4), 8.30 (d, J_{TlH} = 104 Hz, 2 H, $H_{3'}$), 10.80 (s, 1 H, N–H); IR (Nujol) ν(N–H) 3108 (w) cm^{-1}. Anal. Calcd for $(C_{21}H_{32}ClN_2O_{10}Tl)CH_2Cl_2$: C, 33.14; H, 4.30; N, 3.51. Found: C, 33.25; H, 4.59; N, 3.26.

Preparation of (18-Crown-6)(imidazole)(phenyl)thallium(III) Diperchlorate (8). In a 20-mL round-bottomed flask was placed **1** (1.489 g, 2.00 mmol), and the flask was charged with nitrogen. To this were added 5 mL of acetonitrile and imidazole (0.545 g, 8.00 mmol). This solution was stirred at room temperature for 1 h. To the reaction mixture was added 100 mL of diethyl ether to give colorless precipitates. These solids were filtered and washed with 50 mL of diethyl ether. Addition of 100 mL of diethyl ether to an acetonitrile (5 mL) solution of the solids afforded pure **8** as colorless solids in 89% yield (1.443 g, 1.78 mmol): mp 246 °C dec; ^1H NMR (CD_3CN) 3.65 (s, 24 H, 18-crown-6), 7.75 (dd, J_{TlH} = 953 Hz, J_{HH} = 7.0 Hz, 2 H, H_2), 7.65 (dt, J_{TlH} = 377 Hz, J_{HH} = 7.0 Hz, 2 H, H_3), 7.67 (dt, J_{TlH} = 127 Hz, J_{HH} = 8.0 Hz, 1 H, H_4), 8.57 (d, J_{TlH} = 41 Hz, 1 H, $H_{2'}$), 7.14 (d, J_{TlH} = 52 Hz, 1 H, $H_{4'}$), 8.35 (d, J_{TlH} = 41 Hz, 1 H, $H_{5'}$); IR (Nujol) ν(N–H) 3160 (m) cm^{-1}. Anal. Calcd for $C_{21}H_{33}Cl_2N_2O_{14}Tl$: C, 31.03; H, 4.09; N, 3.45. Found: C, 31.39; H, 3.94; N, 3.44.

Preparation of Pentakis(*N*-methylimidazole)(phenyl)thallium(III) Diperchlorate (9). Reactants (**1**, 0.372 g, 0.50 mmol: *N*-methylimidazole, 0.430 g, 5.0 mmol) were resolved in a similar way as in **8**, and the solution was stirred at room temperature for 1 min in the darkness. Colorless solids precipitated. To the reaction mixture was added 100 mL of diethyl ether to enforce precipitation of all amount of the product. The solids obtained were washed with 100 mL of diethyl ether. Addition of 150 mL of diethyl ether to an acetonitrile (30 mL) solution of the solids afforded pure **9** as colorless solids in 90% yield (0.409 g, 0.45 mmol): mp 197 °C dec; ^{1}H NMR (CD$_3$CN) 7.38 (dd, $J_{\mathrm{TlH}} = 903$ Hz, $J_{\mathrm{HH}} = 7.5$ Hz, 2 H, H$_2$), 7.52 (dt, $J_{\mathrm{TlH}} = 335$ Hz, $J_{\mathrm{HH}} = 7.5$ Hz, 2 H, H$_3$), 7.47 (dt, $J_{\mathrm{TlH}} = 116$ Hz, $J_{\mathrm{HH}} = 7.5$ Hz, 1 H, H$_4$), 3.73 (s, 15 H, CH$_3$), 7.60 (s, 5 H, H$_{2'}$), 7.18 (s, 5 H, H$_{4'}$), 6.86 (s, 5H, H$_{5'}$); IR (Nujol) ν(C–O–C and ClO$_4$) 1097 (s) cm^{-1}. Anal. Calcd for (C$_{26}$H$_{35}$Cl$_2$N$_{10}$O$_8$Tl)H$_2$O: C, 34.36; H, 4.10; N, 15.41. Found: C, 34.31; H, 3.88; N, 15.39.

Reaction of 1 with Aniline. Into an acetonitrile-d_3 (0.6 mL) solution of **1** (0.074 g, 0.1 mmol) was added aniline (0.037 g, 0.4 mmol). ^{1}H NMR spectra of the reaction mixture were measured after 20 min at room temperature. The complex **1** completely changed to [Ph(OH)Tl$^{\mathrm{III}}$(18-crown-6)](ClO$_4$).[9]

Reaction of 8 with NaCl in CD$_3$CN/D$_2$O Mixed Solvent. Into an acetonitrile-d_3 (0.5 mL) solution of **8** (0.0816 g, 0.1 mmol) was added a D$_2$O (0.2 mL) solution of NaCl (0.0040 g, 0.1 mmol). An ^{1}H NMR spectrum of the reaction mixture measured after 20 min at room temperature showed that complex **8** completely changed to [Ph(Cl)Tl$^{\mathrm{III}}$(18-crown-6)](ClO$_4$)[13] and free imidazole.

Reaction of 8 with Triethylamine. Into an acetonitrile-d_3 (0.6 mL) solution of **8** (0.0816 g, 0.1 mmol) was added triethylamine (0.0010 g, 0.1 mmol). An ^{1}H NMR spectrum of the reaction mixture measured after 20 min at room temperature showed that complex **8** completely changed to [Ph(OH)Tl$^{\mathrm{III}}$(18-crown-6)](ClO$_4$)[9] and free imidazole.

Reaction of 8 with Pyridine. Into an acetonitrile-d_3 (0.6 mL) solution of **8** (0.0816 g, 0.1 mmol) was added pyridine (0.079 g, 1.0 mmol). An ^{1}H NMR spectrum of the reaction mixture measured after heating at 60 °C for 1 day showed no ligand-exchange reaction.

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Alkyne-Substituted Carbonyl Clusters of Iridium: Synthesis, Characterization, and Solid-State Structures of Ir$_6$(CO)$_{13}$(μ-CO)(μ_3-η^2-PhCCPh) and Ir$_6$(CO)$_{12}$(μ_3-η^2-PhCCPh)$_2$·CH$_2$Cl$_2$

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The carbonyl cluster Ir$_6$(CO)$_{14}$(μ_3-η^2-PhCCPh) (**1**) is obtained by oxidation of [Ir$_6$(CO)$_{15}$]$^{2-}$ with the [Fe(C$_5$H$_5$)$_2$]$^+$ cation, in the presence of diphenylacetylene. Complex **1** crystallizes in the triclinic space group (No. 2) $P\bar{1}$ with $a = 9.443$ (1) Å, $b = 16.622$ (1) Å, $c = 21.560$ (3) Å, $\alpha = 89.87$ (1)°, $\beta = 96.45$ (1)°, $\gamma = 101.78$ (1)°, $V = 3291$ (1) Å^3, and $Z = 4$; $R = 0.034$ for 6236 observed reflections having $I \geq 3\sigma(I)$. When complex **1** is heated with excess of PhC≡CPh, a further substitution occurs, yielding the carbonyl cluster Ir$_6$(CO)$_{12}$(μ_3-η^2-PhCCPh)$_2$ (**2**). Crystals of **2** are monoclinic, space group $C2/c$ (No. 15) with $a = 10.751$ (6) Å, $b = 17.393$ (7) Å, $c = 23.240$ (7) Å, $\beta = 85.42$ (4)°, $V = 4332$ (5) Å^3, and $Z = 4$; $R = 0.028$ for 1645 observed reflections having $I \geq 3\sigma(I)$. Both compounds contain an octahedron of iridium atoms, with the alkynyl units interacting with the faces of the metallic cores, in a μ_3-η^2 fashion.

Introduction

Many efforts are devoted in these days to the preparation of metal carbonyl clusters substituted with small organic fragments, in order to mimic the interactions of such molecules with metallic surfaces.[2] The most intense research is focused on alkyne-substituted clusters, mainly for the metals of group 8 of the periodic table.[3] In contrast, relatively few compounds are known for the metals of the Co subgroup, and these few examples are restricted to clusters of three and four metal atoms.[3] The main reason is probably due to the thermal or photochemical activation methods employed for the synthesis of the alkyne-substituted compounds, with consequent cluster fragmentation or reorganization. For example, when the tetrahedral cluster Ir$_4$(CO)$_{12}$ is irradiated in the presence of C$_2$(CO$_2$Me)$_2$, the rectangular cluster Ir$_4$(CO)$_8$(Me$_2$CO$_2$C$_2$)$_4$ is formed.[4]

When studying the chemistry of iridium clusters, we observed that [Ir$_6$(CO)$_{15}$]$^{2-}$ typically adds 2e-donor ligands (such as halides or CO), when oxidized.[5] Therefore, we exploited the same synthetic approach, which requires very mild conditions, using ligands with different donor capability.[6] We report here the preparation and the solid-state characterization of two new hexanuclear iridium carbonyl clusters containing one and two molecules of diphenylacetylene, respectively.

Results

Synthesis of Ir$_6$(CO)$_{14}$(μ_3-η^2-PhCCPh) (1) and Ir$_6$(CO)$_{12}$(μ_3-η^2-PhCCPh)$_2$ (2). When [Ir$_6$(CO)$_{15}$]$^{2-}$ is oxi-

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