CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF GEORGIA, ATHENS, GEORGIA 30601

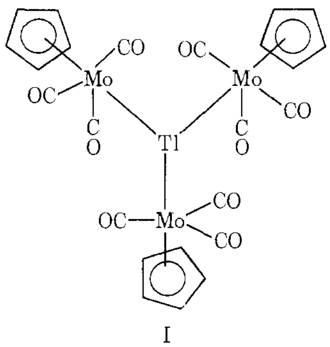
Organometallic Derivatives of the Transition Metals. XXIV. The Formation of a Thallium(III) Derivative in the Reaction between Molybdenum Hexacarbonyl and Thallium Cyclopentadienide[1]

BY R. B. KING[2]

Received February 9, 1970

The most commonly used and generally applicable technique for the synthesis of π-cyclopentadienyl derivatives is the reaction of sodium cyclopentadienide with a transition metal halide.[3] This reaction was first used for the preparation of certain metallocenes in 1956.[4] A more recent variation of this reaction substitutes thallium(I) cyclopentadienide for the sodium cyclopentadienide.[5-9] Thallium(I) cyclopentadienide was found to offer the following advantages over sodium cyclopentadienide: (1) thallium(I) cyclopentadienide is air stable and readily obtained in the pure state; (2) thallium(I) cyclopentadienide undergoes fewer side reactions in certain transition metal systems than sodium cyclopentadienide.

Another type of preparatively useful reaction of sodium cyclopentadienide is its displacement of three carbonyl groups from the metal hexacarbonyls to give the sodium cyclopentadienyltricarbonylmetalates Na[$C_5H_5M(CO)_3$].[10,11] This note describes the analogous reaction of thallium(I) cyclopentadienide with a representative metal hexacarbonyl, $Mo(CO)_6$, in an attempt to prepare thallium(I) cyclopentadienyltricarbonylmolybdate, $[TlMo(CO)_3C_5H_5]_n$. However, an unexpected disproportionation reaction was found to occur which resulted in the formation of the nonionic thallium(III) derivative $Tl[Mo(CO)_3C_5H_5]_3$ (I).



I

Experimental Section

A nitrogen atmosphere was routinely provided for the following operations: (a) carrying out reactions, (b) admitting to evacuated vessels, and (c) handling solutions of $Tl[Mo(CO)_3C_5H_5]_3$. Thallium(I) cyclopentadienide was prepared from thallium(I) sulfate, potassium hydroxide, and cyclopentadiene by the published procedure.[12]

Reaction of Thallium(I) Cyclopentadienide with Hexacarbonylmolybdenum.—A mixture of 2.69 g (10 mmol) of thallium(I) cyclopentadienide, 2.54 g (10 mmol) of hexacarbonylmolydenum, and 75 ml of tetrahydrofuran (freshly distilled over $LiAlH_4$) was boiled under reflux for 15–20 hr. After cooling to room temperature, the deep red reaction mixture was filtered and the residue was washed with a few milliliters of tetrahydrofuran. Tetrahydrofuran was removed from the combined filtrate and washings at 25° (40 mm). The resulting dark red-green crystals were washed with three 20-ml portions of pentane and dried. Unreacted TlC_5H_5 and $Mo(CO)_6$ were removed from this crystalline solid by heating at 45–65° (0.1 mm). The crude $Tl[Mo(CO)_3C_5H_5]_3$ was then extracted with 150 ml of acetone in four portions. The filtered dark red acetone extracts were treated with 40 ml of hexane and the solution was then concentrated to ~10 ml at 40 mm. The resulting red-green crystals were washed by decantation with two 50-ml portions of pentane. The insoluble fluffy yellow decomposition product could be decanted away with each portion of pentane leaving behind the denser red-green crystals of $Tl[Mo(CO)_3C_5H_5]_3$. After drying at 25° (0.1 mm) the yield of dark red-green crystalline $Tl[Mo(CO)_3C_5H_5]_3$ was 0.54–0.93 g (17–30% based on $Mo(CO)_6$, the limiting reagent). *Anal.* Calcd for $C_{24}H_{15}Mo_3O_9Tl$: C, 30.7; H, 1.6; Mo, 30.7; O, 15.3; Tl, 21.8. Found: C, 31.7, 31.9; H, 1.7, 1.6; Mo, 30.7; O, 16.1, 16.2; Tl, 21.0.

Infrared Spectrum.—The following bands were observed on an infrared spectrum taken in a KBr pellet and recorded on a Perkin-Elmer Model 421 spectrometer with grating optics: ν(CH) frequency at 3112 cm^{-1} (vw); ν(CO) frequencies at 1960 (vs), 1945 (vs), and 1885 cm^{-1} (vs); other bands at 1422 (vw), 1413 (w), 1352 (vw), 1347 (vw), 1104 (vw), 1060 (vw), 1052 (w), 1006 (w), 998 (w), 842 (w), 828 (w), 815 (m), 808 (m), 802 (m), 577 (m), 539 (s), 540 cm^{-1} (m, sh).

Proton Nmr Spectrum.—The following π-C_5H_5 resonances (all singlets) were observed in spectra taken in the indicated solvents and recorded on a Varian A-60 or a Perkin-Elmer Hitachi R-20 spectrometer at 60 Mc: (a) acetone, τ 4.52 and 4.64 of approximate relative intensities ~4:1; (b) chloroform, τ 4.61, 4.73, and 4.82 of variable relative intensities (*e.g.*, ~5:4:2); (c) benzene, τ 5.05, 5.16, and 5.41 of relative intensities ~8:8:2; (d) trifluoroacetic acid, τ 4.17 and 4.3 (broad).

Reaction of $NaMo(CO)_3C_5H_5$ with Thallium(I) Sulfate.—A solution of $NaMo(CO)_3C_5H_5$ (~50 mmol) in tetrahydrofuran was prepared by the usual procedure[10,13] and the tetrahydrofuran was removed at 25° (40 mm). The yellow solid residue was dissolved in 100 ml of 10% aqueous sodium hydroxide and the filtered yellow solution treated with a filtered solution of 12.5 g (24.8 mmol) of thallium(I) sulfate in 100 ml of water. A yellow precipitate formed immediately but became deep red upon standing overnight. The precipitate was then filtered, washed with four 20-ml portions of water, and dried. The crude product was purified by extraction with acetone. Evaporation of the filtered acetone extracts followed by washing with pentane gave a ~10% yield of dark red-green crystalline $Tl[Mo(CO)_3C_5H_5]_3$ identical with material obtained from TlC_5H_5 and $Mo(CO)_6$ as described above.

---

[1] Part XXIII: R. B. King and A. Efraty, *J. Organometal. Chem.*, in press.

[2] Fellow of the Alfred P. Sloan Foundation, 1967–1969.

[3] J. M. Birmingham, *Advan. Organometal. Chem.*, **2**, 365 (1964).

[4] G. Wilkinson, F. A. Cotton, and J. M. Birmingham, *J. Inorg. Nucl. Chem.*, **2**, 95 (1956).

[5] (a) A. N. Nesmeyanov, R. B. Materikova, and N. S. Kochetkova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1334 (1963); *Chem. Abstr.*, **59**, 12841*d* (1963); (b) A. N. Nesmeyanov, K. N. Anisimov, and N. E. Kolobova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2220 (1964); *Chem. Abstr.*, **62**, 7788*b* (1965).

[6] C. C. Hunt and J. R. Doyle, *Inorg. Nucl. Chem. Lett.*, **2**, 283 (1966).

[7] J. Powell and B. L. Shaw, *J. Chem. Soc. A*, 583 (1968).

[8] T. J. Katz and J. J. Mrowca, *J. Amer. Chem. Soc.*, **89**, 1105 (1967).

[9] R. B. King, *Inorg. Chem.*, **7**, 90 (1968).

[10] T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956).

[11] E. O. Fischer, W. Hafner, and O. Stahl, *Z. Anorg. Allg. Chem.*, **282**, 47 (1955).

[12] F. A. Cotton and L. T. Reynolds, *J. Amer. Chem. Soc.*, **80**, 269 (1958).

[13] R. B. King and M. B. Bisnette, *J. Organometal. Chem.*, **2**, 15 (1964).

Discussion

If the reaction between hexacarbonylmolybdenum and thallium(I) cyclopentadienide proceeded entirely analogously to the corresponding reaction between hexacarbonylmolybdenum and sodium cyclopentadienide, the product would be thallium(I) cyclopentadienyltricarbonylmolybate, $TlMo(CO)_3C_5H_5$. However, the dark red-green crystalline solid obtained from the reaction between hexacarbonylmolybdenum and thallium(I) cyclopentadienide was shown by elemental analyses on several independent preparations to be the thallium(III) derivative $Tl[Mo(CO)_3C_5H_5]_3$ (I) rather than the expected thallium(I) derivative. Further support for structure I for $Tl[Mo(CO)_3C_5H_5]_3$ with pairs of $C_5H_5Mo(CO)_3$ groups bonded to each other through a thallium atom was obtained from the ν(CO) region of the infrared spectrum where frequencies were observed similar in position and relative intensities to those reported[14] for the mercury derivative $Hg[Mo(CO)_3C_5H_5]_2$ when two $C_5H_5Mo(CO)_3$ groups are bonded to each other through a mercury atom. Furthermore, the ν(CO) frequencies in the infrared spectrum of $Tl[Mo(CO)_3C_5H_5]_3$ do not correspond to those reported[15] for the $C_5H_5Mo(CO)_3^-$ anion. This further supports the nonionic structure I rather than ionic formulations such as $[C_5H_5Mo(CO)_3TlMo(CO)_3C_5H_5]^+[C_5H_5Mo(CO)_3]^-$ with a cation similar to the well-known R_2Tl^+ cations.[16]

The thallium compound $Tl[Mo(CO)_3C_5H_5]_3$ was fairly stable in the solid state but decomposed rather rapidly in solution thereby preventing purification by usual recrystallization techniques. Fortunately, the insoluble decomposition products could be suspended in the mother liquors and decanted away from the crystals of purified $Tl[Mo(CO)_3C_5H_5]_3$. The instability of $Tl[Mo(CO)_3C_5H_5]_3$ in solution also complicated a study of its proton nmr spectrum. Only in acetone solution did $Tl[Mo(CO)_3C_5H_5]_3$ appear to be stable enough to give predominantly (>70%) a single peak (τ 4.52) which could be assigned to the 15 equivalent protons required for structure I. The proton chemical shift of one of the peaks of the decomposition products of $Tl[Mo(CO)_3C_5H_5]_3$ (τ 4.61 in $CHCl_3$ solution) corresponds to that reported[17] for $[C_5H_5Mo(CO)_3]_2$ (τ 4.61 in $CDCl_3$ solution) suggesting the following mode of decomposition in solution

$$Tl[Mo(CO)_3C_5H_5]_3 \rightleftharpoons [C_5H_5Mo(CO)_3]_2 + TlMo(CO)_3C_5H_5$$

The third peak observed in the chloroform and benzene nmr spectra could then arise from the thallium(I) derivative $TlMo(CO)_3C_5H_5$ which reverts to the thallium(III) derivative $Tl[Mo(CO)_3C_5H_5]_3$ upon attempted isolation. The instability of $TlMo(CO)_3C_5H_5$ in the solid state is suggested further by the observation that the yellow precipitate (presumably $TlMo(CO)_3C_5H_5$) obtained by mixing aqueous solutions of $NaMo(CO)_3C_5H_5$ and thallium(I) sulfate rapidly decomposes to give the thallium(III) derivative $Tl[Mo(CO)_3C_5H_5]_3$ upon attempted isolation.

The behavior of $Tl[Mo(CO)_3C_5H_5]_3$ in trifluoroacetic acid solution is quite different. The sharp peak at τ 4.17 appears to arise from the trifluoroacetate $CF_3CO_2Mo(CO)_3C_5H_5$ (lit.[18] value τ 4.12 in acetone solution); the broad resonance at τ 4.3 has not yet been identified.

The compound $Tl[Mo(CO)_3C_5H_5]_3$ is of particular interest since the only previously reported metal carbonyl derivatives with thallium–transition metal bonds are the cobalt compounds $TlCo(CO)_4$ and $Tl[Co(CO)_4]_3$ first prepared by Hieber and Teller[19] by reaction of a mixture of finely divided cobalt and thallium with carbon monoxide under vigorous conditions. Patmore and Graham[20] have studied much more recently the thallium(III) derivative $Tl[Co(CO)_4]_3$ which they prepared either from $NaCo(CO)_4$ and thallium(III) chloride or from $Co_2(CO)_8$ and thallium(I) acetylacetonate; the latter reaction is another example of the formation of a thallium(III) transition metal derivative from a thallium(I) starting material similar to the preparation of the thallium(III) derivative $Tl[Mo(CO)_3C_5H_5]_3$ from thallium(I) cyclopentadienide discussed in this note.

The red-green dichroic appearance of $Tl[Mo(CO)_3C_5H_5]_3$ resembles that of certain solid 16-electron square-planar complexes of rhodium(I) (*e.g.*, $C_5H_7O_2Rh(CO)_2$)[21] and platinum(II) (*e.g.*, $Pt(CN)_4^{2-}$)[22] which can form "stacked" polymeric crystal structures with metal–metal δ bonding on an axis perpendicular to the coordination square.[23] The thallium atom in $Tl[Mo(CO)_3C_5H_5]_3$ apparently has a coordination number of 3 with planar-trigonal sp^2 hybridization. Furthermore, the thallium atom in $Tl[Mo(CO)_3C_5H_5]_3$ has a 16-electron configuration[24] like the central metal atoms in the "stackable" square-planar rhodium(I), iridium(I), and platinum(II) derivatives. The coplanarity of the three thallium–molybdenum bonds and the 16-electron configuration of the three-coordinate thallium atom makes possible a similar stacked polymeric structure for $Tl[Mo(CO)_3C_5H_5]_3$ in the solid state with thallium–thallium bonding between layers. The molybdenum atoms in successive layers would then be relatively close to each other thereby possibly accounting for the facile decomposition in solution to give $[C_5H_5Mo(CO)_3]_2$.

Acknowledgment.—I am indebted to the Air Force of Scientific Research for partial support of this work under Grant AF-AFOSR-1211-67. I also wish to acknowledge the assistance of Mr. Charles Eavenson with some of the nmr experiments.

---

(14) R. D. Fisher and K. Noack, *J. Organometal. Chem.*, **16**, 125 (1969).

(15) R. B. King, K. H. Pannell, C. A. Eggers, and L. W. Houk, *Inorg. Chem.*, **7**, 2353 (1968).

(16) H. M. Powell and D. M. Crowfoot, *Nature*, **130**, 131 (1932): *Z. Kristallogr., Kristallogeometrie, Kristallophys., Kristalchem.*, **87**, 370 (1934).

(17) K. W. Barnett and P. M. Treichel, *Inorg. Chem.*, **6**, 294 (1967).

(18) R. B. King and R. N. Kapoor, *J. Organometal. Chem.*, **15**, 457 (1968).

(19) W. Hieber and U. Teller, *Z. Anorg. Allg. Chem.*, **249**, 43 (1942).

(20) D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, **5**, 1586 (1966).

(21) F. Bonati and G. Wilkinson, *J. Chem. Soc.*, 3156 (1964).

(22) R. M. Bozorth and L. Pauling, *Phys. Rev.*, **39**, 537 (1932); K. Krogmann and H. D. Hausen, *Z. Anorg. Allg. Chem.*, **358**, 67 (1968).

(23) K. Krogmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 35 (1969).

(24) R. B. King, *Advan. Chem. Ser.*, **62**, 203 (1967).