Notes

Study of the Reactivity of $CpMCo(CO)_7$ (M = Mo, W) Complexes toward Various Alkynes

Ramon Yanez,[1] Noël Lugan, and René Mathieu*

Laboratoire de Chimie de Coordination du CNRS, UP 8241 liée par conventions à l'Université Paul Sabatier et à l'Institut National Polytechnique, 205 route de Narbonne, 31077 Toulouse Cedex, France

Received April 4, 1990

Summary: The $CpMCo(CO)_7$ complexes (M = Mo, W) react with alkynes in boiling hexane, leading to $CpMCo(CO)_5(\mu\text{-}\eta^2,\eta^2\text{-}RC{\equiv}CR')$ complexes (M = Mo, R = R' = H, Ph, $SiMe_3$, C(O)OMe; M = Mo, R = H, R' = $SiMe_3$; M = W, R = R' = Ph, C(O)OMe; M = W, R = H, R' = C(O)OMe) in good yield. The $CpMCo(CO)_4(\mu\text{-}\eta^4\text{-}CR^1CR^2CR^3CR^4)$ compounds are obtained in boiling toluene (M = Mo, $R^1 = R^2 = R^3 = R^4$ = H, Ph; M = Mo, $R^1 = R^4$ = C(O)OMe, $R^2 = R^3$ = H; M = Mo, $R^1 = R^2$ = Ph, C(O)OMe, R^3 = C(O)OMe, R^4 = H; M = W, $R^1 = R^2 = R^3 = R^4$ = H, C(O)OMe), only one isomer being observed. More forcing conditions only lead to decomposition.

The reactivity of $Co_2(CO)_8$ or $[CpM(CO)_3]_2$ (M = Cr, Mo, W) complexes toward alkynes is now well-known and well-developed. Except the classical complexes containing the $\mu\text{-}\eta^2,\eta^2$-bonded alkyne,[2] it has been shown that up to three alkynes can be linked between the two metal centers.[2a,3] Curiously, no similar studies have been performed with the readily available mixed dinuclear systems $CpMCo(CO)_7$ (M = Mo, W),[4] which could led to new reactivity or new reactions. This is the reason we have investigated the reactivity of these compounds toward various alkynes. We have observed that these dinuclear complexes can only accommodate up to two alkynes through the intermediate formation of the complexes containing a bridging $\mu\text{-}\eta^2,\eta^2$-alkyne.

Treatment of $CpMCo(CO)_7$ complexes (M = Mo, W) with a stoichiometric amount of alkynes in refluxing hexane affords $CpMCo(CO)_5(RC{\equiv}CR')$ complexes in good yield (40–70%), which have been isolated by chromatography (M = Mo, R = R' = H, Ph, $SiMe_3$, C(O)OMe; M = Mo, R = H, R' = Me_3Si; M = W, R = R' = Ph, C(O)OMe; M = W, R = H, R' = C(O)OMe).

Spectroscopic data are consistent with a structure in which the alkyne bridges the metal–metal bond in a $\mu\text{-}\eta^2,\eta^2$ fashion as in the homodinuclear complexes.[2] The same situation has also been observed for the mixed $NiMCp_2(\mu\text{-}\eta^2,\eta^2\text{-}RC{\equiv}CR)(CO)_2$ compounds.[5]

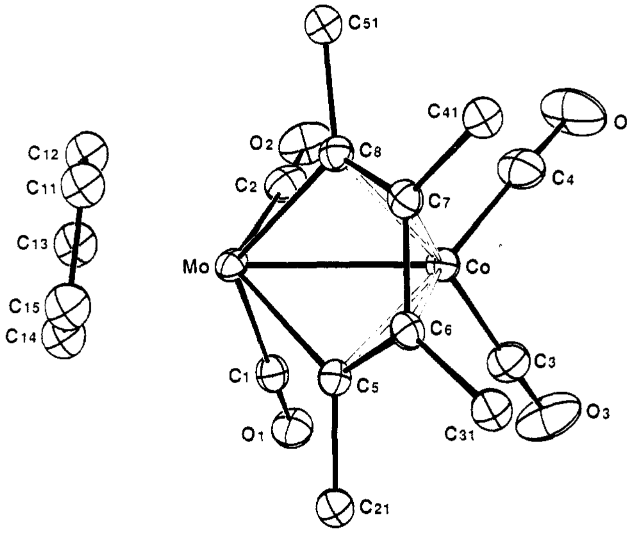


Figure 1. ORTEP plot of $CpMoCo(CO)_4(\mu\text{-}\eta^4\text{-}CPhCPhCPhCPh)$ including the labeling scheme.

In boiling toluene and with 2 equiv of alkyne, the reaction leads to the formation of $CpMCo(CO)_4(RC{\equiv}CR')_2$ complexes, which have been purified by chromatography and isolated in 25–60% yield (M = Mo, R = R' = H, Ph; M = Mo, R = H, R' = C(O)OMe; M = W, R = R' = H, C(O)OMe).

The same compounds have been obtained by starting from $CpMCo(CO)_5(RC{\equiv}CR')$ upon addition of 1 equiv of alkyne, in boiling toluene, allowing us to prepare two complexes containing two different alkynes, $CpMoCo(CO)_4(RC{\equiv}CR')(R^1C{\equiv}CR^2)$ (R = R' = Ph, R^1 = H, R^2 = C(O)OMe)) in 45% and 62% yield, respectively. The spectroscopic data suggest the formation of metallacyclopentadiene rings (especially for R = R' = H). Nevertheless, it was difficult to know which metal was engaged in the ring on this basis alone, since both possibilities could be assumed.[6,7]

Thus, an X-ray structure determination was carried out for $CpMoCo(CO)_4(PhC{\equiv}CPh)_2$. The structure of the compound is given in Figure 1, and bond distances and angles of interest are gathered in Table I. The molecule consists of $CpMo(CO)_2$ and $Co(CO)_2$ units linked by a

---

[1] Present address: Universitat Autonoma de Barcelona, Departament de Quimica (Area 10), 08193 Bellaterra (Barcelona), Spain.

[2] (a) For cobalt, see: Dickson, R. S.; Fraser, P. J. *Adv. Organomet. Chem.* **1974**, *12*, 323 and references therein. (b) For group 6, see: Klingler, R. J.; Butler, W.; Curtis, M. D. *J. Am. Chem. Soc.* **1975**, *37*, 3535. (c) Bailey, W. I.; Chisholm, M. H.; Cotton, F. A.; Rankel, I. A. *J. Am. Chem. Soc.* **1978**, *100*, 5764. (d) Ginley, D. S.; Bock, C. R.; Wrighton, M. S. *Inorg. Chim. Acta* **1977**, *23*, 85.

[3] Knox, S. A. R.; Stansfield, R. F. D.; Stone, F. G. A.; Winter, M. J.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1982**, 173.

[4] Abrahamson, H. B.; Wrighton, M. S. *Inorg. Chem.* **1978**, *17*, 1103.

[5] Chetcuti, M. J.; Eigenbrot, C.; Green, K. A. *Organometallics* **1987**, *6*, 2298.

[6] Davidson, J. L. *J. Chem. Soc., Dalton Trans.* **1983**, 1667.

[7] Yamazaki, H.; Yasufuku, K.; Wakatsuki, Y. *Organometallics* **1983**, *2*, 726.

0276-7333/90/2309-2998$02.50/0

Table I. Bond Distances (Å) and Bond Angles (deg) of Interest for $\mathrm{CpMo(CO)_2Co(CO)_2(\mu\text{-}\eta^4\text{-}C(Ph)C(Ph)C(Ph)C(Ph))\bullet CH_2Cl_2}$ with Esd's in Parentheses

Bond Distances

Mo–Co	2.676 (1)	Co–C(7)	2.130 (3)
Mo–C(1)	2.009 (4)	Co–C(8)	2.042 (3)
Mo–C(2)	1.992 (4)	C(1)–O(1)	1.146 (4)
Mo–C(5)	2.206 (4)	C(2)–O(2)	1.151 (5)
Mo–C(8)	2.187 (3)	C(3)–O(3)	1.142 (4)
Co–C(3)	1.755 (4)	C(4)–O(4)	1.145 (5)
Co–C(4)	1.748 (4)	C(5)–C(6)	1.426 (5)
Co–C(5)	2.000 (3)	C(6)–C(7)	1.427 (5)
Co–C(6)	2.129 (3)	C(7)–C(8)	1.429 (5)

Mo–(η-$\mathrm{C_5H_5}$) range 2.296 (3)–2.379 (3)

Bond Angles

Co–Mo–C(1)	80.7 (1)	C(3)–Co–C(7)	143.8 (2)
Co–Mo–C(2)	75.8 (1)	C(3)–Co–C(8)	171.3 (2)
Co–Mo–C(5)	49.8 (1)	C(4)–Co–C(5)	174.6 (1)
Co–Mo–C(8)	48.4 (1)	C(4)–Co–C(6)	137.0 (2)
C(1)–Mo–C(2)	79.7 (1)	C(4)–Co–C(7)	105.7 (1)
C(1)–Mo–C(5)	77.7 (1)	C(6)–Co–C(7)	39.2 (1)
C(2)–Mo–C(8)	83.0 (1)	Mo–C(1)–O(1)	178.5 (3)
C(5)–Mo–C(8)	72.8 (1)	Mo–C(2)–O(2)	174.0 (3)
Mo–Co–C(3)	118.1 (1)	Co–C(3)–O(3)	176.4 (4)
Mo–Co–C(4)	125.1 (1)	Co–C(4)–O(4)	177.3 (3)
Mo–Co–C(6)	80.7 (1)	Mo–C(5)–C(6)	118.0 (2)
Mo–Co–C(7)	80.5 (1)	C(5)–C(6)–C(7)	114.6 (3)
C(3)–Co–C(4)	89.0 (2)	C(6)–C(7)–C(8)	114.2 (3)
C(3)–Co–C(6)	109.5 (2)	Mo–C(8)–C(7)	118.5 (2)

Mo–Co bond 2.676 (1) Å long and a molybdacyclopentadiene ring derived from two PhC≡CPh molecules. This structure is very similar to that of $\mathrm{CpWCo(CO)_4(CF_3C{\equiv}CCF_3)_2}$, a complex resulting from the reaction of $\mathrm{CpWCl(CF_3C{\equiv}CCF_3)_2}$ with $\mathrm{Co_2(CO)_8}$.[8] The Mo–C(5) and Mo–C(8) bonds are equal, and the cobalt atom is more tightly bonded to the C(5) and C(8) atoms than to the C(6) and C(7) atoms. The carbon–carbon bond distances are equal, within the experimental error, giving evidence of electron delocalization in the metallacyclopentadienyl ring.

Examination of the spectroscopic data of the other synthesized metallacyclopentadiene complexes shows that in the case of dissymmetric alkynes or of two different alkynes only one isomer is observed. Comparison of the proton chemical shift of the CH groups in the $\mathrm{CpMoCo(CO)_4(\mu\text{-}\eta^4\text{-}CR^1CR^2CC(O)OMeCH)}$ complexes when $\mathrm{R^1 = R^2 = C(O)OMe}$, Ph or when $\mathrm{R^1 = C(O)OMe}$, $\mathrm{R^2 = H}$ strongly suggests that in the first case the CH groups are on the metallacycle, in the 2-position, and are in the 3-position in the second case. Indeed, there is about 1 ppm of difference between the two situations and it is known that CH groups directly bonded to metal resonate at lower field.[9] Thus, it appears that in contrast with to the reaction of formation of rhodacyclopentadiene rings, where the CH groups are always found in the 3-position,[9] the regioselectivity of the coupling reactions in the Mo–Co bimetallic system is probably the result of a competition between electronic and steric factors.

In contrast with the case of the homodinuclear complexes,[2a,3] it was not possible to induce the coupling of a third molecule of alkyne. More forcing conditions only led to decomposition.

To conclude, the use of mixed $\mathrm{CpMCo(CO)_7}$ systems has not put in evidence a new reactivity toward alkynes compared to that of the $\mathrm{Co_2(CO)_8}$ and $\mathrm{[CpM(CO)_3]_2}$ complexes. This is perhaps the consequence of a more polar and less stable metal–metal bond. (The formation of $\mathrm{CpM(CO)_3^-}$ has been observed in some experiments by infrared monitoring of the reaction mixture.)

Experimental Section

All experiments were performed under a nitrogen atmosphere with use of standard Schlenk-tube techniques. IR spectra were recorded in hexane solution, on a Perkin-Elmer 225 machine. ^{1}H NMR spectra were obtained on a Bruker AC200 instrument in deuterated chloroform solutions.

The $\mathrm{CpMCo(CO)_7}$ (M = Mo, W) complexes were prepared according to published procedures.[4]

Synthesis of $\mathrm{CpMCo(CO)_5(R^1C{\equiv}CR^2)}$ Complexes. $\mathrm{CpMCo(CO)_7}$ complexes (100 mg; M = Mo, W) and the stoichiometric amount of the alkyne were heated under reflux in hexane for 1 h. (In the case of acetylene, the solution was saturated by bubbling at room temperature and the reaction performed under an acetylene atmosphere.) The reaction mixture was then evaporated to dryness, and the residue was chromatographed on a silica gel column. Elution with hexane first gave traces of the starting material and then the $\mathrm{CpMCo(CO)_5(R^1C{\equiv}CR^2)}$ complexes, which were recrystallized in a $\mathrm{CH_2Cl_2}$/hexane mixture. The following compounds were isolated.

$\mathrm{CpMoCo(CO)_5(PhC{\equiv}CPh)\cdot 0.15CH_2Cl_2}$: orange crystals in 60% yield. Anal. Calcd for $\mathrm{C_{24.15}H_{15.3}Cl_{0.3}O_5CoMo}$: C, 50.66; H, 2.75. Found: C, 50.34; H, 2.74. IR: ν(CO) 2043 m, 1998 s, 1940 w cm^{-1}. ^{1}H NMR: 7.28 (Ph), 5.35 (Cp) ppm.

$\mathrm{CpMoCo(CO)_5(HC{\equiv}CH)}$: green crystals in 40% yield. Anal. Calcd for $\mathrm{C_{12}H_7O_5CoMo}$: C, 37.33; H, 1.83. Found: C, 36.97; H, 2.10. IR: ν(CO) 2029 m, 1987 s, 1965 s, 1915 w cm^{-1}. ^{1}H NMR: 5.26 (Cp), 3.76 (CH) ppm.

$\mathrm{CpMoCo(CO)_5(MeOC(O)C{\equiv}CC(O)OMe)}$: orange crystals in 70% yield. Anal. Calcd for $\mathrm{C_{16}H_{11}O_9CoMo}$: C, 38.27; H, 2.21. Found: C, 38.31: H, 2.14. IR: ν(CO) 2065 m, 2028 s, 2005 sh, 1995 s, 1970 w cm^{-1}. ^{1}H NMR: 5.45 (Cp), 3.78 (OMe) ppm.

$\mathrm{CpMoCo(CO)_5(Me_3SiC{\equiv}CH)}$: orange crystals in 65% yield. Anal. Calcd for $\mathrm{C_{15}H_{15}O_5SiCoMo}$: C, 39.32; H, 3.30. Found: C, 38.64; H, 3.34. IR: ν(CO) 2048 m, 2000 s, 1980 s, 1945 m cm^{-1}. ^{1}H NMR: 6.12 (CH), 5.38 (Cp), 0.16 ($\mathrm{SiMe_3}$) ppm.

$\mathrm{CpMoCo(CO)_5(Me_3SiC{\equiv}CSiMe_3)}$: orange crystals in 62% yield. Anal. Calcd for $\mathrm{C_{18}H_{23}O_5Si_2CoMo}$: C, 40.76; H, 4.37. Found: C, 40.57; H, 4.33. IR: ν(CO) 2038 m, 1990 s, 1970 s, 1925 m cm^{-1}. ^{1}H NMR: 5.37 (Cp), 0.27 ($\mathrm{SiMe_3}$) ppm.

$\mathrm{CpWCo(CO)_5(PhC{\equiv}CPh)}$: orange crystals in 60% yield. Anal. Calcd for $\mathrm{C_{24}H_{15}O_5CoW}$: C, 46.04; H, 2.41. Found: C, 45.79; H, 2.38. IR: ν(CO) 2042 m, 1997 s, 1975 s, 1932 m cm^{-1}. ^{1}H NMR: 7.27 (Ph), 5.45 (Cp) ppm.

$\mathrm{CpWCo(CO)_5(MeOC(O)C{\equiv}CC(O)OMe)}$: orange crystals in 65% yield. Anal. Calcd for $\mathrm{C_{16}H_{11}O_9CoW}$: C, 32.57; H, 1.88. Found: C, 32.35; H, 2.01. IR: ν(CO) 2065 m, 2022 s, 2000 s, 1970 m cm^{-1}. ^{1}H NMR: 5.50 (Cp), 3.77 (OMe) ppm.

$\mathrm{CpWCo(CO)_5(MeOC(O)C{\equiv}CH)}$: orange crystals in 67% yield. Anal. Calcd for $\mathrm{C_{16}H_9O_7CoW}$: C, 31.69: H, 1.71. Found: C, 31.69; H, 1.70. IR: ν(CO) 2057 m, 2010 s, 1988 s, 1948 m cm^{-1}. ^{1}H NMR: 5.67 (CH), 5.49 (Cp), 3.72 (OMe) ppm.

Synthesis of $\mathrm{CpMCo(CO)_4(R^1CCR^2)(R^3CCR^4)}$ Complexes. (a) $\mathrm{R^1 = R^2 = R^3 = R^4}$. $\mathrm{CpMCo(CO)_7}$ complexes (100 mg; M = Mo, W) and 2 equiv of the alkyne were heated under reflux in toluene for 1 h. Chromatography on a silica gel column with hexane as eluent gave the complexes, which were recrystallized in a $\mathrm{CH_2Cl_2}$/hexane mixture. The following complexes have been isolated.

$\mathrm{CpMoCo(CO)_4(HC{\equiv}CH)_2}$: yellow crystals in 25% yield. Anal. Calcd for $\mathrm{C_{13}H_9O_4CoMo}$: C, 40.65; H, 2.36. Found: C, 40.43; H, 2.18. IR: ν(CO) 2027 s, 1968 s, 1920 w cm^{-1}. ^{1}H NMR: 7.09, 6.77 (AA′BB′ system, $\mathrm{(CH)_4}$), 4.99 (Cp) ppm.

$\mathrm{CpMoCo(CO)_4(PhC{\equiv}CPh)_2\cdot CH_2Cl_2}$: orange crystals in 60% yield. Anal. Calcd for $\mathrm{C_{38}H_{27}Cl_2O_4CoMo}$: C, 59.01; H, 3.52. Found: C, 59.35; H, 3.49. IR: ν(CO) 2018 s, 1970 sh, 1960 s, 1925 w cm^{-1}. ^{1}H NMR: 6.95 (Ph), 5.01 (Cp) ppm.

$\mathrm{CpMoCo(CO)_4(MeOC(O)C{\equiv}CH)_2}$: yellow crystals in 65% yield. Anal. Calcd for $\mathrm{C_{17}H_{13}O_8CoMo}$: C, 40.82; H, 2.62. Found: C, 40.53; H, 2.52. IR: ν(CO) 2040 s, 1985 m, 1950 w cm^{-1}. ^{1}H

---

[8] Davidson, J. L.; Manojlovic-Muir, L.; Muir, K. W.; Keith, A. N. *J. Chem. Soc., Chem. Commun.* **1980**, 749.

[9] Dickson, R. S.; McLure, F. I.; Nesbit, R, J. *J. Organomet. Chem.* **1988**, *349*, 413 and references therein.

Table II. Experimental Data for the X-ray Study of the Compound $CpMo(CO)_2Co(CO)_2(\mu\text{-}\eta^4\text{-}C(Ph)C(Ph)C(Ph)C(Ph))\bullet CH_2Cl_2$

compd	$CpMo(CO)_2Co(CO)_2(\mu\text{-}\eta^4\text{-}C(Ph)C(Ph)C(Ph)C(Ph))\cdot CH_2Cl_2$
formula	$C_{53}H_{39}Cl_2O_6CoMo$
fw	783.50
a, Å	9.742 (1)
b, Å	11.082 (1)
c, Å	15.805 (2)
α, deg	90.53 (1)
β, deg	98.92 (1)
γ, deg	102.45 (1)
V, Å^3	1644 (5)
Z	2
ρ_{calcd}, g cm^{-3}	1.582
space group	C_i^1-$P\bar{1}$
t, °C	−155
radiation	graphite monochromated, Mo Kα, λ(Mo Kα_1) = 0.7093 Å
linear abs coeff, cm^{-1}	9.99
transmission factors^a	0.924–0.999
receiving aperture, mm	3.5 × 3.5
takeoff angle, deg	2.75
scan speed, deg min^{-1}	2
scan mode	ω–2θ
scan range, deg	0.9 below Kα_1 to 0.9 above Kα_2
2θ limit, deg	2–50
no. of unique data used in final refinement, $F_o^2 > 3\sigma(F_o^2)$	5286
final no. of variables	213
R (on F_o, $F_o^2 > 3\sigma(F_o^2)$)^b	0.040
R_w (on F_o, $F_o^2 > 3\sigma(F_o^2)$)^c	0.041
error in observn of unit weight, e^2	1.40

^{a} ψ-scan method. ^{b} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{c} $R_w = [\sum w(|F_o| - |F_c|)^2/(\sum w|F_o|^2)]^{1/2}$ (unit weights).

NMR: 6.28 (CH), 5.08 (Cp), 3.70 (OMe) ppm.

$CpWCo(CO)_4(MeOC(O)C{\equiv}CC(O)OMe)_2$: yellow crystals in 60% yield. Anal. Calcd for $C_{21}H_{17}O_{12}CoW$: C, 35.82; H, 2.43. Found: C, 36.40; H, 2.63. IR: ν(CO) 2048 s, 1998 m, 1950 w cm^{-1}. ^1H NMR: 5.26 (Cp), 3.81, 3.68 (OMe) ppm.

$CpWCo(CO)_4(HC{\equiv}CH)_2$: yellow crystals in 30% yield. Anal. Calcd for $C_{13}H_9O_4CoW$: C, 33.08; H, 1.92. Found: C, 33.03; H, 1.89. IR: ν(CO) 2023 s, 1962 m, 1910 w cm^{-1}. ^1H NMR: 6.85, 6.70 (AA′BB′ system, $(CH)_4$), 5.08 (Cp) ppm.

(b) $R^1 = R^2$, $R^3 \neq R^4$. $CpMoCo(CO)_5(R^1C{\equiv}CR^2)$ complexes (50 mg) and 1 equiv of $MeOC(O)C{\equiv}CH$ were heated under reflux in toluene for 1 h. Chromatography on a silica gel column with hexane as eluent gave the complexes, which were recrystallized in hexane. The following complexes have been isolated.

$CpMoCo(CO)_4(PhC{\equiv}CPh)(MeOC(O)C{\equiv}CH)$: yellow crystals in 45% yield. Anal. Calcd for $C_{27}H_{19}O_6CoMo$: c, 54.57; H, 3.22. Found: C, 54.12; H, 3.18. IR: ν(CO) 2030 s, 1975 m, 1950 w cm^{-1}. ^1H NMR: 7.14 (CH), 7.05 (Ph), 4.91 (Cp), 3.75 (OMe) ppm.

$CpMoCo(CO)_4(MeOC(O)C{\equiv}CC(O)OMe)(MeOC(O)C{\equiv}CH)$: yellow crystals in 62% yield. Anal. Calcd for $C_{19}H_{15}O_{10}CoMo$: C, 40.88; H, 2.71. Found: C, 40.62; H, 2.63. IR: ν(CO) 2049 s, 1998 m, 1962 w cm^{-1}. ^1H NMR: 7.22 (CH), 5.13 (Cp), 3.83, 3.73, 3.71 (OMe) ppm.

Structure Determination of $CpMoCo(CO)_4(PhC{\equiv}CPh)_2\cdot CH_2Cl_2$. Data were collected at 123 K on an Enraf-Nonius CAD4 diffractometer equipped with a low-temperature device.[10] Cell constants were obtained by least-squares refinement of the setting angles of 25 automatically centered reflections in the range 24° < 2θ < 28° with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Experimental data for the X-ray study are gathered in Table II.

A total of 5286 reflections ($I > 3\sigma(I)$) were used for structure solution with a combination of the SDP crystallographic computing package[11] and the SHELX-76 package.[12]

Table III. Fractional Atomic Coordinates and Isotropic or Equivalent Temperature Factors (Å × 100) with Esd's in Parentheses

atom	x/a	y/b	z/c	U_{eq}/U_{iso}
Mo(1)	0.10081 (3)	0.73268 (3)	0.34887 (2)	1.83 (5)
Co(2)	0.06527 (5)	0.60597 (4)	0.19923 (3)	1.70 (7)
C(1)	−0.0189 (4)	0.5722 (3)	0.3786 (2)	2.4 (5)
O(1)	−0.0891 (3)	0.4821 (2)	0.3963 (2)	3.2 (4)
C(2)	−0.0905 (4)	0.7480 (3)	0.2902 (2)	2.9 (6)
O(2)	−0.2030 (3)	0.7606 (3)	0.2631 (2)	4.2 (5)
C(3)	−0.0214 (4)	0.4492 (3)	0.1933 (2)	2.8 (6)
O(3)	−0.0845 (3)	0.3491 (3)	0.1884 (2)	4.8 (6)
C(4)	−0.0489 (4)	0.6278 (3)	0.1066 (3)	3.1 (6)
O(4)	−0.1259 (4)	0.6372 (3)	0.0458 (2)	5.1 (6)
C(5)	0.2148 (3)	0.5959 (3)	0.3085 (2)	1.8 (5)
C(6)	0.2882 (3)	0.6226 (3)	0.2372 (2)	1.7 (5)
C(7)	0.2635 (3)	0.7297 (3)	0.1931 (2)	1.7 (5)
C(8)	0.1635 (3)	0.7876 (3)	0.2254 (2)	1.7 (5)
C(11)	0.2680 (2)	0.9160 (2)	0.4012 (2)	2.90 (8)
C(12)	0.1283 (2)	0.9304 (2)	0.4069 (2)	3.23 (8)
C(13)	0.0715 (2)	0.8443 (2)	0.4653 (2)	3.54 (9)
C(14)	0.1761 (2)	0.7767 (2)	0.4958 (2)	3.39 (9)
C(15)	0.2976 (2)	0.8210 (2)	0.4562 (2)	3.08 (8)
C(21)	0.2337 (3)	0.4804 (2)	0.3571 (1)	2.04 (7)
C(22)	0.2733 (3)	0.4919 (2)	0.4460 (1)	2.93 (8)
C(23)	0.2966 (3)	0.3894 (2)	0.4920 (1)	3.60 (9)
C(24)	0.2802 (3)	0.2754 (2)	0.4491 (1)	3.38 (9)
C(25)	0.2406 (3)	0.2638 (2)	0.3602 (1)	3.06 (8)
C(26)	0.2173 (3)	0.3664 (2)	0.3143 (1)	2.45 (7)
C(31)	0.3840 (2)	0.5475 (2)	0.2075 (1)	1.82 (7)
C(32)	0.5072 (2)	0.5368 (2)	0.2623 (1)	2.63 (8)
C(33)	0.6012 (2)	0.4725 (2)	0.2342 (1)	3.33 (9)
C(34)	0.5721 (2)	0.4189 (2)	0.1513 (1)	3.22 (8)
C(35)	0.4488 (2)	0.4297 (2)	0.0966 (1)	2.65 (8)
C(36)	0.3548 (2)	0.4940 (2)	0.1247 (1)	2.13 (7)
C(41)	0.3388 (2)	0.7739 (2)	0.1192 (1)	1.78 (6)
C(42)	0.2643 (2)	0.7876 (2)	0.0384 (1)	2.29 (7)
C(43)	0.3383 (2)	0.8276 (2)	−0.0286 (1)	2.67 (8)
C(44)	0.4869 (2)	0.8539 (2)	−0.0148 (1)	2.89 (8)
C(45)	0.5614 (2)	0.8402 (2)	0.0661 (1)	2.84 (8)
C(46)	0.4874 (2)	0.8002 (2)	0.1331 (1)	2.28 (7)
C(51)	0.1386 (2)	0.9070 (2)	0.1865 (2)	1.99 (7)
C(52)	0.0058 (2)	0.9212 (2)	0.1456 (2)	2.93 (8)
C(53)	−0.0092 (2)	1.0343 (2)	0.1118 (2)	3.76 (9)
C(54)	0.1086 (2)	1.1332 (2)	0.1188 (2)	3.42 (9)
C(55)	0.2413 (2)	1.1190 (2)	0.1597 (2)	2.79 (8)
C(56)	0.2564 (2)	1.0059 (2)	0.1935 (2)	2.28 (7)
Cl(1)	0.3630 (2)	0.8348 (1)	0.72157 (9)	6.2 (2)
Cl(2)	0.3602 (2)	1.0613 (1)	0.63328 (8)	7.4 (3)
C	0.2757 (6)	0.9555 (5)	0.6993 (4)	6 (1)

The positions of Mo and Co atoms were determined by direct methods. All remaining non-hydrogen atoms were located by the usual combination of full-matrix least-squares refinement and difference electron density syntheses. The compound was found to crystallize with 1 mole of dichloromethane/mol of complex. Atomic scattering factors were taken from the usual tabulations.[13] Anomalous dispersion terms for Mo and Co atoms were included.[14] An empirical absorption correction was applied.[15] The final refinements were conducted with use of the SHELX-76 program. All non-hydrogen atoms were allowed to vibrate anisotropically, except carbon atoms of cyclopentadienyl and phenyl rings, which were refined as isotropic rigid groups in order to reduce the number of variable parameters (C_5H_5, C–C = 1.420 Å; C_6H_5, C–C = 1.395 Å). Hydrogen atoms were entered in idealized positions (C–H = 0.97 Å) and held fixed during refinements. The final full-matrix least-squares refinement converged to R = 0.040 and R_w = 0.041 with unit weights.

Final atomic coordinates and U_{eq} × 100 (or U_{iso} × 100) values for non-hydrogen atoms are given in Table III.

---

(10) Bonnet, J. J.; Askenazy, S. Commercially available as NJET from Soterem, ZI de Vic, 31320 Castanet Tolosan, France.

(11) Enraf-Nonius Structure Determination Package, 4th ed.; B. A. Frenz and Associates: College Station, TX, and Enraf-Nonius: Delft, The Netherlands, 1981.

(12) Sheldrick, G. M. SHELX-76 Program for Crystal Structure Determination; University of Cambridge: Cambridge, England, 1976.

(13) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. 4, Table 2.2B.

(14) Reference 13, Table 2.3.1.

(15) North, A. C. T.; Philipps, D. C.; Mathews, F. S. *Acta Crystallogr.* 1968, *A24*, 351.

Acknowledgment. R.Y. thanks the CNRS for financial support for a postdoctoral position.

Registry No. $\mathrm{CpMoCo(CO)_7}$, 62015-65-0; $\mathrm{CpWCo(CO)_7}$, 62015-64-9; $\mathrm{CpMoCo(CO)_5(PhC{\equiv}CPh)}$, 129540-85-8; $\mathrm{CpMoCo(CO)_5(HC{\equiv}CH)}$, 129540-86-9; $\mathrm{CpMoCo(CO)_5(MeOC(O)C{\equiv}CC(O)OMe)}$, 129540-87-0; $\mathrm{CpMoCo(CO)_5(Me_3SiC{\equiv}CH)}$, 129540-88-1; $\mathrm{CpMoCo(CO)_5(Me_3SiC{\equiv}CSiMe_3)}$, 129540-89-2; $\mathrm{CpWCo(CO)_5(PhC{\equiv}CPh)}$, 119705-21-4; $\mathrm{CpWCo(CO)_5(MeOC(O)C{\equiv}CC(O)OMe)}$, 129540-90-5; $\mathrm{CpWCo(CO)_5(MeOC(O)C{\equiv}CH)}$, 129540-91-6; $\mathrm{CpMoCo(CO)_4(HC{\equiv}CH)_2}$, 129540-92-7; $\mathrm{CpMoCo(CO)_4(PhC{\equiv}CPh)_2{\cdot}CH_2Cl_2}$, 129540-94-9; $\mathrm{CpMoCo(CO)_4(MeOC(O)C{\equiv}CH)_2}$, 129540-95-0; $\mathrm{CpWCo(CO)_4(MeOC(O)C{\equiv}CC(O)OMe)_2}$, 129540-96-1; $\mathrm{CpWCo(CO)_4(HC{\equiv}CH)_2}$, 129540-97-2; $\mathrm{CpMoCo(CO)_4(PhC{\equiv}CPh)(MeOC(O)C{\equiv}CH)}$, 129540-98-3; $\mathrm{CpMoCo(CO)_4(MeOC(O)C{\equiv}CC(O)OMe)(MeOC(O)C{\equiv}CH)}$, 129540-99-4; $\mathrm{CpMoCo(CO)_4(PhC{\equiv}CPh)_2}$, 129540-93-8; $\mathrm{PhC{\equiv}CPh}$, 501-65-5; $\mathrm{HC{\equiv}CH}$, 74-86-2; $\mathrm{MeOC(O)C{\equiv}CC(O)Me}$, 762-42-5; $\mathrm{Me_3SiC{\equiv}CH}$, 1066-54-2; $\mathrm{Me_3SiC{\equiv}CSiMe_3}$, 14630-40-1; $\mathrm{MeOC(O)C{\equiv}CH}$, 922-67-8.

Supplementary Material Available: A listing of anisotropic thermal parameters (1 page); a table of calculated and observed structure factors (26 pages). Ordering information is given on any current masthead page.

C-Methylated (Germacyclopentadienyl)lithium

Pascal Dufour,[†] Jacques Dubac,*[,‡] Michèle Dartiguenave,*[,†] and Yves Dartiguenave[†]

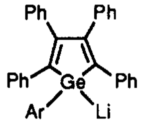
Laboratoire de Chimie Inorganique and Laboratoire des Organométalliques, Associé au CNRS, URA 477, Université Paul-Sabatier, 118 route de Narbonne, 31062 Toulouse Cedex, France

Received February 22, 1990

Summary: (1-Phenyl-2,3,4,5-tetramethyl-1-germacyclopentadienyl)lithium (**4**) was prepared by reaction of 1-phenyl-2,3,4,5-tetramethylgermole with *n*-butyllithium in THF/hexane at −70 °C and chemically identified by electrophilic silylation and stannylation. A ^{13}C NMR suggests that the negative charge in **4** is strongly localized on the germanium atom.

The characterization of silabenzenes[1,2] and anions derived from silacyclopentadienes,[3-5] compounds having Hückel π systems, represents important work in the area of p_π–p_π multiple bonding of the heavier main-group elements.

In the case of the silacyclopentadienide anion, the theoretical approach reveals a pyramidal ground-state structure and very low resonance energy.[6] Three silyl anions derived from C-phenylated siloles or dibenzosiloles have been characterized in solution,[3-5] but the synthesis of a C-methylated species failed.[7] Therefore, it appears that the stability of these ions requires phenyl group substituents on the ring carbon atoms. Until now, the same result has been observed for germanium chemistry; only C-phenylated derivatives of (germacyclopentadienyl)lithium (**1a–c**) were known.[8,9]



1

Ar = phenyl (**1a**),[8] tolyl (**1b**), *p*-(dimethylamino)phenyl (**1c**)[9]

We report here the characterization of the first C-methylated group 14 metallacyclopentadienide, (1-phenyl-2,3,4,5-tetramethyl-1-germacyclopentadienyl)lithium (4).

Experimental Section

The starting germole 2 has been prepared from bis(cyclopentadienyl)zirconium dichloride, 2-butyne, and germanium tetrachloride.[10]

Ether and tetrahydrofuran were freshly distilled from sodium wire and benzophenone. All manipulations were carried out under argon by using conventional Schlenk-tube techniques.

Proton and carbon NMR spectra (200 and 50.32 MHz) were recorded on a Bruker AC 200 spectrometer (δ in ppm from TMS).

1-Phenyl-2,3,4,5-tetramethylgermole (3). To 100 mL of a cooled (−70 °C) solution of 2 g (7.95 mmol) of germole 2 in dry $\mathrm{Et_2O}$ was added 50 mL of phenylmagnesium bromide (7.95 mmol) in $\mathrm{Et_2O}$. The solution, warmed to room temperature, was stirred for 2 h and slowly added to a cooled (0 °C) suspension of 0.3 g (7.95 mmol) of $\mathrm{LiAlH_4}$ in 20 mL of $\mathrm{Et_2O}$. The mixture was stirred for 5 h. After hydrolysis and extractions ($\mathrm{Et_2O}$), the organic solution was concentrated. Distillation gave 3 (1.65 g) in 80% yield: bp 102 °C (0.52 mmHg); ^{1}H NMR ($\mathrm{C_6D_6}$) δ 1.98 and 1.80 (2 s, CMe), 5.82 (s, GeH), 7.21 and 7.55 (aromatic protons); ^{13}C NMR, see Table I; IR 2031 cm^{-1} (ν(Ge–H)); GC/MS (70 eV; *m/e*, ^{74}Ge) M$^+$ 260 (24), (M − Ph)$^+$ 183 (13), (GePh)$^+$ 151 (100), (M − Ph − $\mathrm{C_2Me_2}$)$^+$ 129 (24). Anal. Calcd for $\mathrm{C_{14}H_{18}Ge}$: C, 64.95; H, 7.00. Found: C, 65.0; H, 7.1.

(1-Phenyl-2,3,4,5-tetramethyl-1-germacyclopentadienyl)lithium (4) and 1-Deuterio-1-phenyl-2,3,4,5-tetramethylgermole (5). A solution of 6.4 mmol of *n*-butyllithium (1.6 M in hexane) was added dropwise to a stirred solution of 1.65 g (6.4 mmol) of hydrogermole 3 in THF (10 mL) cooled to −70 °C. A bright yellow color appeared upon initial addition of butyllithium. The mixture was stirred at −70 °C for 1 h. A solution of 4, prepared from 2 mmol of 3, in THF-d_8 was analyzed by using carbon NMR spectroscopy at −60 °C (Table I).

Deuteriolysis of an aliquot of the THF solution of 4 gives the 1-deuteriogermole 5: ^{1}H NMR ($\mathrm{C_6D_6}$) δ 2.04 and 1.87 (2 s, CMe), 7.27 and 7.58 (aromatic protons); IR 1459 cm^{-1} (ν(Ge–D)); GC/MS (70 eV; *m/e*, ^{74}Ge) M$^+$ 261 (72), (M − Ph)$^+$ 184 (17), (GePh)$^+$ 151

[†] Laboratoire de Chimie Inorganique.

[‡] Laboratoire des Organométalliques.

(1) Raabe, G.; Michl, J. *Chem. Rev.* 1985, *85*, 419 and references therein.

(2) (a) Welsh, K. M.; Rich, J. D.; West, R.; Michl, J. *J. Organomet. Chem.* 1987, *325*, 105. (b) Sekiguchi, A.; Gillette, G. R.; West, R. *Organometallics* 1988, *7*, 1226. (c) Märkl, G.; Schlosser, W.; Sheldrick, W. S. *Tetrahedron Lett.* 1988, *29*, 467. (d) Märkl, G.; Schlosser, W. *Angew, Chem., Int. Ed. Engl.* 1988, *27*, 963. (e) Jutzi, P.; Meyer, M.; Reisenauer, H. P.; Maier, G. *Chem. Ber.* 1989, *122*, 1227 and references therein.

(3) Han, B. H.; Boudjouk, P. *Chungnam Kwahak Yonguchi* 1984, *11*, 101.

(4) Corriu, R. J. P.; Guérin, C.; Kolani, B. *Bull. Soc. Chim. Fr.* 1985, 973.

(5) Ishikawa, M.; Tabohashi, T.; Ohashi, H.; Kumada, M.; Iyoda, J. *Organometallics* 1983, *2*, 351.

(6) (a) Damewood, J. R., Jr. *J. Org. Chem.* 1986, *51*, 5028. (b) Gordon, M. S.; Boudjouk, P.; Anwari, F. *J. Am. Chem. Soc.* 1983, *105*, 4972.

(7) Béteille, J. P.; Laporterie, A.; Dubac, J. *Organometallics* 1989, *8*, 1799.

(8) (a) Curtis, M. D. *J. Am. Chem. Soc.* 1967, *89*, 4241. (b) *Ibid.* 1969, *91*, 6011.

(9) Jutzi, P.; Karl, A. *J. Organomet. Chem.* 1981, *215*, 19.

(10) Fagan, P. J.; Nugent, W. A. *J. Am. Chem. Soc.* 1988, *110*, 2310.

0276-7333/90/2309-3001$02.50/0