Journal of Organometallic Chemistry, 482 (1994) 63-66

Synthesis and coordination chemistry of tellurium alkynes

Holger Keller [a], Jean Claude Daran [b] and Heinrich Lang [a]

[a] *Ruprecht-Karls-Universität, Anorganisch-Chemisches Institut, Im Neuenheimer Feld 270, 69120 Heidelberg (Germany)*
[b] *Université Pierre et Marie Curie, Laboratoire de Chimie des Metaux de Transition 4, Place Jussieu, 75230 Paris Cedex 05 (France)*

(Received December 13, 1993)

Abstract

The reaction of (2,4,6-$Me_3C_6H_2$)TeBr (**I**) with LiC≡CR (R = C_6H_5 : **IIa**; R = $SiMe_3$: **IIb**) gives excellent yields of the tellurium alkynes (2,4,6-$Me_3C_6H_2$)TeC≡CR (R = C_6H_5 : **IIIa**; R = $SiMe_3$: **IIIb**). Compound **IIIb** reacts with octacarbonyl dicobalt (**IV**) to yield the side-on coordinated complex (2,4,6-$Me_3C_6H_2$)Te[(η^2-C≡CSiMe$_3$)$Co_2(CO)_6$] (**V**). The identity of compounds **III** and **V** have been established from analytical and spectroscopic (IR, ^{1}H-, ^{13}C-NMR) data and an X-ray diffraction study of **V**.

Key words: Tellurium; Alkynes; Cobalt; Carbonyl; Crystal structure

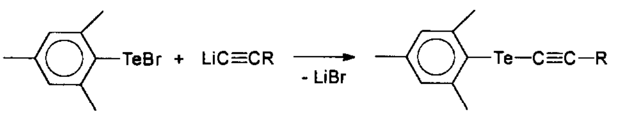
1. Introduction

Organotellurium compounds have attracted interest as potential reagents and intermediates in organic synthesis [1], but tellurium alkynes of the type R′TeC≡CR (R′, R = singly bonded organic ligand) have been little studied [2]. To our knowledge, nothing is known of the ability of these compounds to coordinate with organometallic carbonyl species. Here, we describe the synthesis of the compounds (2,4,6-$Me_3C_6H_2$)TeC≡CR, with R = C_6H_5 or $SiMe_3$, and their reaction with $Co_2(CO)_8$.

2. Results and Discussion

2.1. *Synthesis of (2,4,6-$Me_3C_6H_2$)TeC≡CR (III)*

The compounds (2,4,6-$Me_3C_6H_2$)TeC≡CR (R = C_6H_5 : **IIIa**; R = $SiMe_3$: **IIIb**) can be readily obtained in high yield from the reaction of equimolar amounts of (2,4,6-$Me_3C_6H_2$)TeBr (**I**) and LiC≡CR (R = C_6H_5 : **IIa**; R = $SiMe_3$: **IIb**) in THF at 25°C. Filtration of the solution, evaporation of the solvent in high vacuum, and recrystallization of the residue from *n*-pentane at −30°C affords analytically pure **III**. Compounds **III** are stable towards air for a short period of time, but prolonged exposure to light results in decomposition. The alkyne ligands in **III** show a weak absorption band at 2143 (**IIIa**) or 2073 (**IIIb**) cm^{-1} in the ν(C≡C) region of the IR spectra (see Experimental section). The ^{1}H-NMR (**IIIa, IIIb**) and ^{13}C-NMR (**IIIa**) spectra are consistent with the formulation of compounds **III** as alkyne-substituted tellurium species.

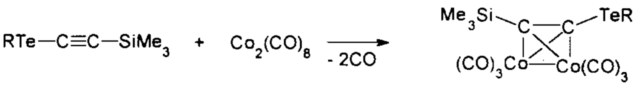


I II III

IIIa: R = C_6H_5
IIIb: R = $SiMe_3$

2.2. *Synthesis of (2,4,6-$Me_3C_6H_2$)Te[(η^2-C≡CSiMe$_3$) $Co_2(CO)_6$] (V)*

The compound (2,4,6-$Me_3C_6H_2$)TeC≡CSiMe$_3$ (**IIIb**) reacts with an equimolar amount of $Co_2(CO)_8$ (**IV**) in *n*-pentane/toluene (1 : 1) at 25°C to give the complex (2,4,6-$Me_3C_6H_2$)Te[(η^2-C≡CSiMe$_3$)$Co_2(CO)_6$] (**V**); the yield is 45%.



IIIa IV V

R = 2,4,6-$Me_3C_6H_2$

Compound **V** can best be purified by evaporation of the solvent, extraction of the reaction residue with *n*-pentane, and column chromatography on silica gel with *n*-pentane/toluene mixtures. Removal of the solvents under high vacuum and recrystallization of the

---

Correspondence to: Priv. Doz. Dr. H. Lang.

0022-328X/94/$7.00
SSDI 0022-328X(94)24632-S

brown residue from n-pentane at $-30°C$ gives dark crystals of **V**. Characterization of **V** is based on analytical and spectroscopic data. The IR spectrum of **V** in the $\nu(CO)$ region shows four strong bands, which are typical for the $Co_2(CO)_6$ organometallic building block [3]. As a result of the side-on coordination of the trimethylsilylethynyl ligand to the $Co_2(CO)_6$ fragment the $\nu(C{\equiv}C)$ absorption band is shifted from 2073 in **IIIb** to 1600 cm^{-1} in **V**. The X-ray diffraction study confirmed the proposed structure of **V** (see Fig. 1).

The structure of **V** is related to that of other complexes of type $[(\eta^2\text{-}RC{\equiv}CR')Co_2(CO)_6]$ [3], $R_nE[(\eta^2\text{-}C{\equiv}CR')Co_2(CO)_6]_{3-n}$ (E = P, As; $n = 0$, 1, 2) [3,4], $(PhC{\equiv}C)E[(\eta^2\text{-}C{\equiv}CPh)Co_2(CO)_6]$ (E = S, Se) [5] or $R_nE[(\eta^2\text{-}C{\equiv}CR')Co_2(CO)_6]_{4-n}$ (E = C, Si, Ge, Sn; n = 0, 1, 2, 3) [6]. In **V** the tellurium trimethylsilylethynyl building block is side-on coordinated via the C_2 unit to a $Co_2(CO)_6$ fragment to form a cobalt-carbon tetrahedrane cluster unit (Fig. 1). Through the side-on coordination of the $Me_3SiC{\equiv}C$ ligand to $Co_2(CO)_6$ the carbon–carbon bond distance is lengthened from approximately 120 pm to 131 pm in **V** (Fig. 1). This is consistent with the corresponding distances in many π-coordinated alkyne complexes [3–6]. Similar observations are apply to the cobalt–cobalt bond length (246.5 pm, Fig. 1).

3. Experimental section

All reactions were carried out under nitrogen using standard Schlenk techniques.

3.1. *Synthesis of $(2,4,6\text{-}Me_3C_6H_2)TeC{\equiv}CR$ (R = Ph: **IIIa**; R = $SiMe_3$: **IIIb**)*

A freshly prepared solution of $LiC{\equiv}CR$ in THF [5b] (R = C_6H_5: 20 mmol; R = $SiMe_3$: 20 mmol) was added dropwise at 0°C to a THF (30 ml) solution of $(2,4,6\text{-}Me_3C_6H_2)TeBr$ (6.53 g; 20 mmol). The mixture immediately turned dark red. It was stirred for 20 min at 0°C and then for 30 min at 25°C. The solvent was evaporated under reduced pressure and the dark red residue extracted with n-pentane/ether (1/1). The extracts were filtered through a pad of Celite. Evaporation of the solvent under reduced pressure and recrystallization of the residue from n-pentane at $-30°C$ gave compound **III**.

IIIa: Yield: 6.40 g (92% based on used **I**). Found: C, 58.69; H, 4.68; $C_{17}H_{16}Te(347.92)$ calc.: C, 58,69; H, 4.64%.-M.p.: 88°C.-IR (n-pentane, CaF_2-cells): $\nu(C{\equiv}C)$: 2143 cm^{-1}. ^1H-NMR ($[D_6]$-acetone): 2.30 (s, 6 H, o-CH_3), 2.65 (s, 3 H, p-CH_3), 6.88 (s, 2 H, C_6H_2), 7.3-7.6 (m, 5 H, C_6H_5). $^{13}C\{^1H\}$-NMR ($[D_6]$-acetone): 20.7 (s, 1 C, p-CH_3), 28.0 (s, 2 C, o-CH_3), 110.1 (s, 1 C,

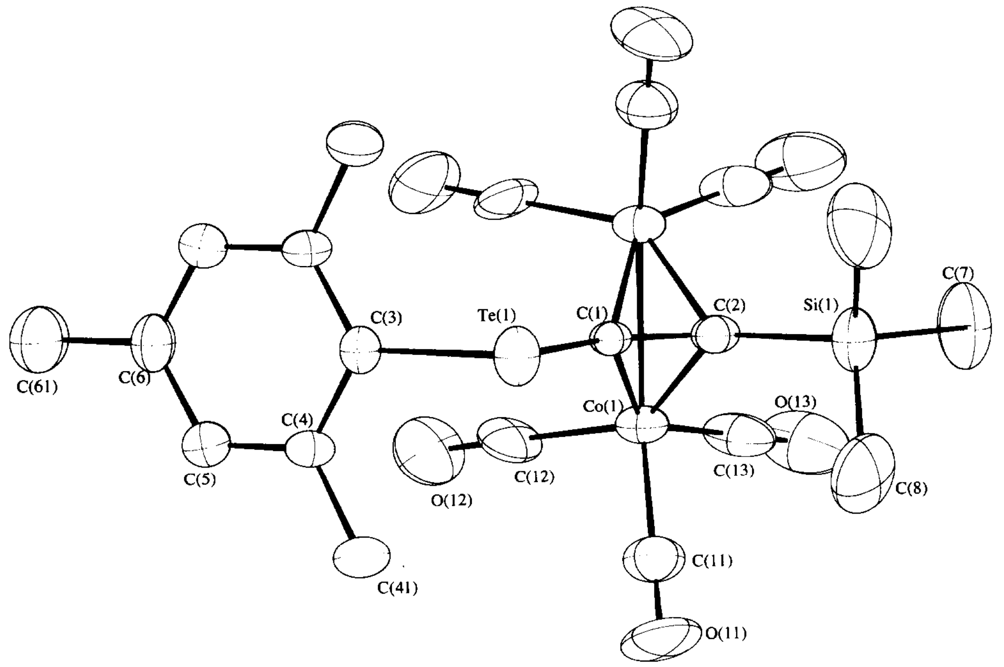


Fig. 1. Molecular geometry and atom labeling scheme for $(2,4,6\text{-}Me_3C_6H_2)Te[(\eta^2\text{-}C{\equiv}CSiMe_3)Co_2(CO)_6]$ (**V**). Selected bond distances (pm) and angles (deg): Co(1)–Co(2) 246.5(2), C(1)–C(2) 131(1), C(1)–Te(1) 206.5(8), C(3)–Te(1) 231.1(9), C(2)–Si(1) 186.8(9), C(1)–Te(1)–C(3) 98.3(3), Te(1)–C(1)–C(2) 135.6(6), C(1)–C(2)–Co(2) 77.3(3).

C≡C), 119.3 (s, 1 C, C≡C), 124.4, 128.4, 129.0, 132.1, 138.6, 140.1, 144.6, 145.1 (s, 12 C, C_6H_5/C_6H_2).

IIIb: Yield: 5.30 g (77% based on used **I**). Found: C, 48.89; H, 6.05; $C_{14}H_{20}TeSi$ (344.00) calc.: C, 48.88; H, 5.86%.-M.p.: 127°C. IR (*n*-pentane, CaF_2-cells): ν(C≡C): 2073 cm^{-1}. ^1H-NMR ($CDCl_3$): 0.14 (s, 9 H, $SiMe_3$), 2.33 (s, 6 H, *o*-CH_3), 2.61 (s, 3 H, *p*-CH_3), 6.85 (s, 2 H, C_6H_2).

3.2. Synthesis of $(2,4,6\text{-}Me_3C_6H_2)Te[(\eta^2\text{-}C{\equiv}CSiMe_3)Co_2(CO)_6]$ (V)

IIIb (500 mg, 1.45 mmol) was dissolved at 25°C in *n*-pentane/toluene (1 : 1, 80 ml) and treated dropwise with a equimolar amount of a $Co_2(CO)_8$ (**IV**) *n*-pentane/toluene (1 : 1) solution (20 ml). Carbon monoxide was evolved and the colour changed to brown olive. The mixture was stirred at 25°C for 2 h, the volatile materials were removed under high vacuum, and the residue purified by column chromatography (column size: 20 × 2.5 cm^2; −20°C; *n*-pentane; silica gel). Elution with *n*-pentane/toluene mixtures (10 : 1-5 : 1) gave a dark brown zone, and removal of the solvent from the eluate and recrystallization of the residue from *n*-pentane at −30°C gave dark brown crystals of $(2,4,6\text{-}Me_3C_6H_2)Te[(\eta^2\text{-}C{\equiv}C\text{-}SiMe_3)Co_2(CO)_6]$. Yield: 400 mg (44% based on used **IIIb**).

TABLE 1. Crystallographic data

Crystal parameters	
Formula	$C_{20}H_{20}Co_2O_6SiTe$
F.W.	629.93
Crystal system	orthorhombic
Space group	*Pmcn*
a (Å)	12.928(2)
b (Å)	10.343(1)
c (Å)	18.947(4)
V (Å^3)	2533(1)
Z	4
ρ (calcd), g cm^{-3}	1.651
μ (Mokα) cm^{-1}	25.15
Data collection	
Diffractometer	CAD4F
Monochromator	graphite
Radiation	Mokα(0.71070)
Scan type	$\omega/2\theta$
Scan range θ, deg	0.8 + 0.34 tan θ
2θ range (°)	3–56
Reflctn collected	3455
Reflctn used ($I > 3\sigma(I)$)	1778
Refinement	
R	0.0395
R_w	0.0385
Abs. corr.	Difabs
Min./max. abs.	0.97–1.03
Weighting scheme	unity
L.s. parameters	149

TABLE 2. Atomic coordinates and isotropic thermal parameters with esd values in parantheses

Atom	*x*	*y*	*z*	$U_{(eq)}$
Co(1)	0.15464(6)	0.15910(9)	0.96875(5)	0.0534
Te(1)	0.2500	0.22419(6)	0.78500(3)	0.0646
Si(1)	0.2500	0.4789(3)	0.9645(2)	0.0802
C(1)	0.2500	0.2166(8)	0.8939(4)	0.0408
C(2)	0.2500	0.3018(8)	0.9451(5)	0.0511
C(3)	0.2500	0.0216(8)	0.7645(4)	0.0534
C(4)	0.1557(5)	−0.0444(6)	0.7563(3)	0.0559
C(41)	0.0526(6)	0.021(1)	0.7618(6)	0.0822
C(5)	0.1567(5)	−0.1762(7)	0.7414(4)	0.0650
C(6)	0.2500	−0.2401(9)	0.7331(5)	0.0664
C(61)	0.2500	−0.381(1)	0.716(1)	0.1051
C(7)	0.2500	0.511(2)	1.0588(9)	0.1232
C(8)	0.134(1)	0.548(1)	0.9217(7)	0.1191
C(11)	0.0349(6)	0.2196(8)	0.9350(4)	0.0803
O(11)	−0.0399(4)	0.2587(7)	0.9124(3)	0.1033
C(12)	0.1359(6)	−0.0101(8)	0.9502(5)	0.0743
O(12)	0.1230(5)	−0.1150(6)	0.9377(4)	0.1097
C(13)	0.1327(5)	0.1770(9)	1.0610(4)	0.0786
O(13)	0.1172(5)	0.1930(8)	1.1199(3)	0.1201

Found: C, 38.01; H, 3.26; $C_{20}H_{20}Co_6O_6SiTe$ (629.93) calc.: C, 38.13; H, 3.20%.-M.p.: 99°C (decomp.).-IR (*n*-pentane, CaF_2-cells): ν(CO): 2085s, 2049vs, 2026vs, 2018vs, 2009m, 1975vw cm^{-1}.-^1H-NMR($CDCl_3$): 0.26(s, 9 H, $SiMe_3$), 2.27(s, 3 H, *p*-CH_3), 2.67(s, 6 H, *o*-CH_3), 6.99(s, 2 H, C_6H_2).

3.3. Crystal data

A selected crystal was set up on an automatic diffractometer. Unit cell dimensions with estimated standard deviations were obtained from least-square refinements of the setting angles of 25 well centered reflections. Two standard reflections were monitored periodically; they showed no change during data collection. Crystallographic data and other pertinent informations are summarized in Table 1. Corrections were made for Lorentz and polarization effects. Empirical absorption corrections (Difabs) [7] were applied.

Computations were performed by using CRYSTALS [8] adapted on a Micro Vax II. Atomic form factors for neutral Te, Co, Si, O, C, and H atoms were taken from ref. 9. Anomalous dispersion was taken into account. The structure was solved by direct methods using the SHELX86 [10] program. The hydrogen atoms were found on difference electron density maps but they were introduced in the refinement as fixed contributors in calculated positions. Their atomic coordinates were recalculated after each cycle. They were given isotropic thermal parameters 20% higher than those of the carbon to which they were attached. H atoms attached to the methyl in para position of the Ar group are disordered. Anisotropic temperature factors were introduced for all non-hydrogen atoms. Full matrix least-squares refinements were carried out by minimizing the function $|\Sigma w(|F_o| - |F_o|)^2$, where F_o and F_c are the observed and calculated structure factors. Models reached convergence with $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$ having values listed in Table 1. Criteria for a satisfactory complete analysis were the ratios of rms shift standard deviation being less than 0.1 and no significant features in final difference maps. Atomic coordinates are given in Table 2. A complete list of bond lengths and angles and a table of thermal parameters, have been deposited at the Cambridge Crystallographic Data Centre.

Acknowledgements

We are grateful to the "Deutsche Forschungsgemeinschaft", "Fond der Chemischen Industrie" and Prof. Dr. G. Huttner for supporting this work. We thank Dr. O.J. Curnow for many discussions.

References and notes

1 N. Petragnani and J.V. Comasetto, *Synthesis*, (1986) 1.

2 M.J. Dabdoub and J.V. Comasseto, *Organometallics*, *7* (1988) 84 and references cited therein.

3 For example (a) H. Lang and L. Zsolnai, *Chem. Ber.*, *124* (1991) 259 and references cited therein; (b) R.S. Dickson and P.J. Fraser, *Adv. Organomet. Chem.*, *12* (1974) 323; (c) H.A. Patel, A.J. Carty and N.K. Hota, *J. Organomet. Chem.*, *50* (1973) 247.

4 (a) H. Lang and L. Zsolnai, *Z. Naturforsch., Teil B*, *45* (1990) 1529; (b) P.H. Bird and A.R. Fraser, *J. Chem. Soc., Chem. Commun.*, (1970) 681.

5 (a) M. Herres, O. Walter, H. Lang, R. Hosch and J. Hahn, *J. Organomet. Chem.* *466* (1994) 237; (b) H. Lang, H. Keller, W. Imhof and S. Martin, *Chem. Ber.*, *123* (1990) 417.

6 For example: H. Lang, U. Lay and M. Weinmann, *J. Organomet. Chem.*, *436* (1992) 265 and references cited therein.

7 N. Walker and S. Stuart, *Acta Crystallogr.*, *39* (1983) 158.

8 D.F. Watkin, J.R. Carruthers and P.W. Betteridge, CRYSTALS, *An Advanced Crystallographic Program System*, Chemical Chrystallography Laboratory, University of Oxford, Oxford, 1988.

9 *International Tables for X-ray Crystallography*, vol. IV, Kynoch Press, Birmingham, 1974.

10 G.M. Sheldrick, SHELXS 86, *Program for Crystal Structure Solution*, University of Göttingen, Göttingen, 1986.