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Hexacarbonyldicobalt addition across the C≡C bond of the alkynethiolate ligand in the cluster $[Ru_3(\mu_3,\eta^2\text{-C}{\equiv}\text{CSiMe}_3)(\mu\text{-SC}{\equiv}\text{CSiMe}_3)(CO)_9]$

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Key indicators

Single-crystal X-ray study
T = 180 K
Mean σ(C–C) = 0.005 Å
Disorder in solvent or counterion
R factor = 0.032
wR factor = 0.094
Data-to-parameter ratio = 15.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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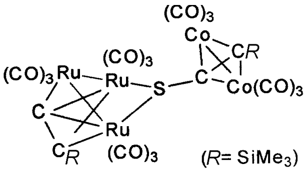
The structure of the title compound, μ_3,η^2-trimethylsilylethynyl-μ-trimethylsilylethynethiolato-pentadecacarbonyldicobalttriruthenium, $[Ru_3Co_2(\mu_3,\eta^2\text{-C}{\equiv}\text{CSiMe}_3)(\mu\text{-SC}{\equiv}\text{C-SiMe}_3)(CO)_{15}]$, consists of an open triangular Ru_3 framework with the acetylide ligand σ-bonded to one Ru atom and π-bonded to the other two Ru atoms. Additionally, the $SC{\equiv}CSiMe_3$ ligand, which has a $Co_2(CO)_6$ fragment coordinated to the C≡C bond, bridges the two terminal Ru atoms of the triangle to give a dimetallatetrahedrane structure.

Comment

Octacarbonyldicobalt has been used as protecting group for C≡C bonds. Adams *et al.* (1993) have prepared clusters $[\{M_3(CO)_{11}\}\{\mu\text{-PPh}_2[C_2Co_2(CO)_6]C_2PPh_2\}]$ (M = Ru, Os), in which the $Co_2(CO)_6$ moiety is linked to the C≡C bond present in the bridging ligand $(PPh_2)_2(C{\equiv}C)$. On the other hand, the compound $S(C{\equiv}CPh)_2$ reacts with one or two equivalents of $Co_2(CO)_8$ to afford the mono- or dicoordinated compounds $(PhC{\equiv}C)S[\eta^2\text{-}(C{\equiv}CPh)Co_2(CO)_6]$ and $S[(\eta^2\text{-}C{\equiv}CPh)_2Co_2(CO)_6]_2$, respectively (Herres *et al.*, 1994). We have studied the addition of the $Co_2(CO)_6$ fragment to the cluster $[Ru_3(CO)_9(\mu_3,\eta^2\text{-C}{\equiv}\text{CSiMe}_3)(\mu\text{-SC}{\equiv}\text{CSiMe}_3)]$, in order to increase its nuclearity. We report herein the synthesis and crystal structure of the new compound $[Ru_3(CO)_9(\mu_3,\eta^2\text{-C}{\equiv}\text{CSiMe}_3)(\mu\text{-SC}{\equiv}\text{CSiMe}_3)Co_2(CO)_6]$, (I). The ^{1}H NMR data are similar to those reported for the compound $[Ru_3(CO)_9(\mu_3,\eta^2\text{-C}{\equiv}\text{CSiMe}_3)(\mu\text{-SC}{\equiv}\text{CSiMe}_3)]$ (Alcalde *et al.*, 2001). The presence of the coordinated $Co_2(CO)_6$ group, as well as the ν(CO) pattern of the $Ru_3(CO)_9$ framework, are observed in the IR spectrum. The positive FAB mass spectrum exhibits the M^+-2CO, $M^+-Co_2(CO)_6$ and several other peaks corresponding to the sequential loss of CO ligands. Suitable crystals for X-ray diffraction studies of compound (I) were obtained from CH_2Cl_2/MeOH at 253 K.



(I)

The structure of (I) consists of an open triangular Ru_3 framework with the alkynethiolate ligand bridging the two Ru atoms of the open edge, and the acetylide ligand σ-bonded to one Ru atom and π-bonded to the other two Ru atoms (Fig. 1). The Ru—Ru bond distances [2.8231 (5) and 2.8344 (4) Å] are similar to those found in $\{[Ru_3(CO)_9(\mu\text{-SC}_2H_5)(\mu,\eta^2\text{-C}{\equiv}CR)]$, with R = CH_3 [2.843 (1) and (2.847(1) Å], R = Ph

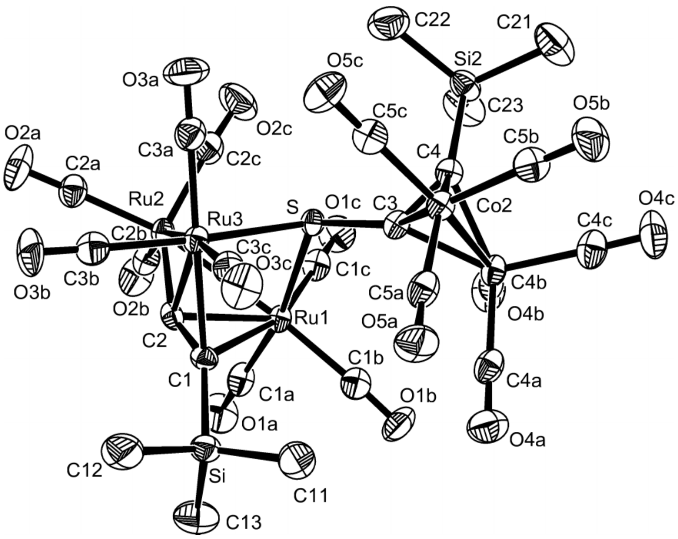


Figure 1

The molecular structure of (I), with ellipsoids at the 50% probability level. H atoms have been omitted.

[2.8391 (8) and 2.8524 (8) Å] (Jeannin *et al.*, 1994), and to those found in [Ru$_3$(CO)$_9$(μ_3,η^2-C$\equiv$CSiMe$_3$)(μ-SC$\equiv$CSiMe$_3$)] [2.8397 (5) and 2.8204 (5) Å; Alcalde *et al.*, 2001]. In addition, the Ru—S distances [2.4331 (7) and 2.4276 (8) Å] are comparable to those found in the starting compound [Ru$_3$(CO)$_9$(μ_3,η^2-C$\equiv$CSiMe$_3$)(μ-SC$\equiv$CSiMe$_3$)] [2.4353 (7) and 2.4373 (7) Å; Alcalde *et al.*, 2001]. As a consequence of the addition of the Co$_2$(CO)$_6$ fragment to the SC$\equiv$CSiMe$_3$ ligand giving a dimetallatetrahedrane structure, it may be noted that the C3—C4 distance [1.356 (4) Å] is greater than in [Ru$_3$(CO)$_9$(μ-SC$\equiv$CSiMe$_3$)(μ_3,η^2-C$\equiv$CSiMe$_3$)] [1.201 (4) Å; Alcalde *et al.*, 2001]. Additionally, the Co1—Co2 bond length of 2.4751 (6) Å, as well as the distances from the Co atoms to the C3—C4 bond [1.958 (2), 1.917 (2), 1.970 (2) and 1.973 (2) Å], are in the ranges expected for this type of coordination (Low *et al.*, 1999; Wadepohl *et al.*, 1996; Herres *et al.*, 1994). Finally, a strong deviation from linearity is observed in the angles S—C3—C4 [125.16 (18)°] and C3—C4—Si [140.26 (18)°], compared with those found in the starting compound [175.7 (2) and 178.3 (2)°, respectively].

Experimental

A mixture of [Ru$_3$(CO)$_9$(μ_3,η^2-C$\equiv$CSiMe$_3$)(μ-SC$\equiv$CSiMe$_3$)] (0.1 g, 0.13 mmol) and Co$_2$(CO)$_8$ (0.088 g, 0.26 mmol) in THF (15 ml) was stirred for 8 h at room temperature. The volatiles were removed under vacuum and *n*-hexane (2 × 15 ml) was added. When the solvent was partially removed, Co$_4$(CO)$_{12}$ precipitated. The resulting solution was dried under vacuum to afford the title compound as a deep-red solid (0.12 g, 0.11 mmol, 86%). Crystals suitable for X-ray study were obtained from CH$_2$Cl$_2$/MeOH (1:1) at 253 K. Analysis calculated for C$_{25}$H$_{18}$Co$_2$O$_{15}$Ru$_3$SSi$_2$ (found): C 28.14 (27.77), H 1.76 (1.90)%. IR (hexane, cm^{-1}): ν(CO): 2097 (*w*), 2082 (*m*), 2070 (*s*), 2058 (*s*), 2050 (*m*), 2033 (*m*), 2015 (*s*), 1994 (*w*), 1986 (*w*). ^{1}H NMR (CDCl$_3$): δ 0.56 (*s*, 9H, SiMe$_3$), 0.30 (*s*, 9H, SiMe$_3$). FAB$^+$ (*m*/*z*): 1011 (M^+-2CO), 929, 901, 875, 845, 817 (M^+-nCO, n = 5–9), 785 [M^+-5CO$-$Co(CO)$_3$], 757 [M^+-6CO$-$Co(CO)$_3$], 696 [M^+-5CO$-$Co$_2$(CO)$_6$].

Crystal data

[Ru$_3$Co$_2$(C$_5$H$_9$Si)(C$_5$H$_9$SSi)(CO)$_{15}$]
M_r = 1067.7
Triclinic, $P\overline{1}$
a = 9.2407 (10) Å
b = 12.0579 (13) Å
c = 18.841 (2) Å
α = 75.882 (13)°
β = 87.813 (14)°
γ = 69.403 (12)°
V = 1903.2 (4) Å^3

Z = 2
D_x = 1.863 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8000 reflections
θ = 2.3–26.1°
μ = 2.19 mm^{-1}
T = 180 (2) K
Parallelepiped, red
0.25 × 0.25 × 0.13 mm

Data collection

Stoe IPDS diffractometer
φ scans
Absorption correction: multi-scan (Blessing, 1995)
$T_{\min}$ = 0.624, $T_{\max}$ = 0.752
18 747 measured reflections
6954 independent reflections

6294 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.031
$\theta_{\max}$ = 26.2°
$h = -10 \rightarrow 10$
$k = -14 \rightarrow 14$
$l = -23 \rightarrow 23$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.094
S = 1.11
6954 reflections
439 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0562P)^2 + 2.2163P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 0.76 e Å^{-3}
$\Delta\rho_{\min}$ = −0.77 e Å^{-3}

Table 1

Selected geometric parameters (Å, °).

Ru1—C2	2.239 (4)	Ru3—C1	2.341 (3)
Ru1—C1	2.344 (4)	Ru3—S1	2.4268 (10)
Ru1—S1	2.4327 (9)	Co1—Co2	2.4748 (8)
Ru1—Ru2	2.8227 (6)	S1—C3	1.778 (3)
Ru2—Ru3	2.8346 (5)	C1—C2	1.275 (5)
Ru3—C2	2.240 (3)	C3—C4	1.348 (5)
Ru1—Ru2—Ru3	72.925 (13)	C4—C3—S1	125.6 (3)
Ru3—S1—Ru1	87.56 (3)	C3—C4—Si2	140.0 (3)

H atoms were located in a difference Fourier map, but were then introduced in idealized positions, with C—H = 0.96 Å and $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(C); riding-model constraints included the torsion angle as a free variable. A final difference synthesis indicated some residual electron densities which might be due to disordered solvent molecules. Attempts to model these densities using CH$_2$Cl$_2$ molecules failed. Owing to the diffuse features of the electron density, we used the BYPASS/SQUEEZE procedure (van der Sluis & Spek, 1990) to mask the disordered solvent region.

Data collection: *IPDS software* (Stoe & Cie, 1996); cell refinement: *IPDS software*; data reduction: *XRED* (Stoe & Cie, 1996); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97 and *WinGX* (Farrugia, 1999).

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m208 Esther Delgado *et al.* • [Ru$_3$Co$_2$(C$_5$H$_9$Si)(C$_5$H$_9$SSi)(CO)$_{15}$] *Acta Cryst.* (2003). E**59**, m207–m209

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Acta Cryst. (2003). E**59**, m207–m209 Esther Delgado *et al.* • $[Ru_3Co_2(C_5H_9Si)(C_5H_9SSi)(CO)_{15}]$ **m209**