

Metal-stabilised diynyl radicals: structure and reactivity of $[\text{Mo}(\text{C}\equiv\text{C}-\text{C}\equiv\text{CSiMe}_3)\text{L}_2(\eta\text{-C}_7\text{H}_7)]^+$, ($\text{L}_2 = 2,2'$ -bipyridine or dppe).

Neil J. Brown, David Collison, Ruth Edge, Emma C. Fitzgerald, Paul J. Low, Madeleine Helliwell, Yien T. Ta and Mark W. Whiteley.

ELECTRONIC SUPPLEMENTARY INFORMATION

Preparations

Synthesis of $[\text{Mo}(\text{C}\equiv\text{C}-\text{C}\equiv\text{CSiMe}_3)(\text{bipy})(\eta\text{-C}_7\text{H}_7)][\text{PF}_6]$, **[1]**PF₆

A purple solution of $[\text{Mo}(\text{C}\equiv\text{C}-\text{C}\equiv\text{CSiMe}_3)(\text{bipy})(\eta\text{-C}_7\text{H}_7)]$, **1**, (0.494g, 1.06 mmol) in dichloromethane (20 cm³) was cooled to -40°C and treated with $[\text{FeCp}_2][\text{PF}_6]$ (0.352g, 1.06 mmol). After stirring for 1h. at -40°C, the resulting orange red solution was warmed to room temperature and then filtered and reduced in volume to 5 cm³ *in vacuo*. Addition of diethylether resulted in precipitation of **[1]**PF₆ as an orange-red solid. The crude product was washed with toluene (2 x 10 cm³) and diethylether (1 x 10cm³) and then recrystallised from CH₂Cl₂/ diethylether. Yield 0.384 g, (59% based on **1**).

Synthesis of $[\{\text{Mo}(\text{dppe})(\eta\text{-C}_7\text{H}_7)\}_2\{\mu\text{-C}=\text{C}(\text{C}\equiv\text{CSiMe}_3)\text{C}(\text{C}\equiv\text{CSiMe}_3)=\text{C}\}][\text{PF}_6]_2$, **[3]**[PF₆]₂

A green solution of $[\text{Mo}(\text{C}\equiv\text{C}-\text{C}\equiv\text{CSiMe}_3)(\text{dppe})(\eta\text{-C}_7\text{H}_7)]$, **2a**, (0.402g, 0.57 mmol) in dichloromethane (30 cm³) was treated with $[\text{FeCp}_2][\text{PF}_6]$ (0.233g, 0.70 mmol). After stirring for 2h., the resulting purple solution was filtered and reduced in volume to 5 cm³ *in vacuo*. Addition of diethylether resulted in precipitation of **[3]**[PF₆]₂ as a deep purple solid. The crude product was washed with toluene (2 x 10 cm³) and diethylether (1 x 10cm³) and then recrystallised from CH₂Cl₂/ diethylether. Yield 0.415 g, (85% based on **2a**).

Spectroscopic and Analytical data

$[\text{Mo}(\text{C}\equiv\text{C}-\text{C}\equiv\text{CSiMe}_3)(\text{bipy})(\eta\text{-C}_7\text{H}_7)][\text{PF}_6]$, **[1]**PF₆

IR spectrum (CH₂Cl₂), $\nu(\text{C}\equiv\text{C})$, cm⁻¹: 2158, w, 2117, w, 1998, m.

Accurate mass, mass spectroscopy: C₂₄H₂₄MoN₂Si requires 466.0767; found: 466.0754.

Microanalysis: C₂₄H₂₄MoN₂SiPF₆ requires: C, 47.3%, H, 3.9%, N, 4.6%. Found: C, 46.1%, H, 3.7%, N, 4.3%.

To confirm microanalytical data for complexes of this type, a derivative of **[1]**PF₆, $[\text{Mo}(\text{C}\equiv\text{C}-\text{C}\equiv\text{CSiMe}_3)(\text{Bu}^t\text{bipy})(\eta\text{-C}_7\text{H}_7)][\text{PF}_6]$ (Bu^tbipy = 4,4'-Bu^t-2,2'-bipyridyl) was prepared, its identity confirmed by IR and EPR spectroscopy and a satisfactory microanalysis obtained. C₃₂H₄₀MoN₂SiPF₆ requires: C, 53.3%, H, 5.5%, N, 3.9%. Found: C, 53.2%, H, 5.7%, N, 3.8%.



IR spectrum (CH_2Cl_2), $\nu(\text{C}\equiv\text{C})$, cm^{-1} : 2120.

Accurate mass, mass spectroscopy: $\text{C}_{80}\text{H}_{80}\text{Mo}_2\text{P}_4\text{Si}_2$ (+2) requires 707.1438; found 707.1442. $\text{C}_{80}\text{H}_{80}\text{Mo}_2\text{P}_4\text{Si}_2\text{PF}_6$ (+1) requires 1559.2600; found 1559.2559.

Microanalysis: $\text{C}_{80}\text{H}_{80}\text{Mo}_2\text{P}_4\text{Si}_2$ [PF_6]₂ requires: C, 56.4%, H, 4.7%. Found: C, 55.6%, H, 4.5%.

^1H NMR (CD_2Cl_2) 300 MHz: 7.75-7.03, m, 40H, Ph(dppe); 4.82, s, 14H, C_7H_7 ; 2.91, br, 8H, CH_2 (dppe); 0.00, s, 18H, SiMe_3 .

^{13}C NMR (CD_2Cl_2), 100 MHz: 374.8, t, J(P-C) 30Hz, $\text{Mo}=\text{C}_\alpha$; 137.6-125.4, 105.3, Ph (dppe) and $\text{C}_\beta\text{-C}_\delta$, $\text{Mo}=\text{C}=\text{C}_\beta\text{-C}_\gamma\equiv\text{C}_\delta\text{-SiMe}_3$; 93.9, C_7H_7 ; 29.0, CH_2 (dppe); -0.3, SiMe_3 .

^{31}P NMR (CD_3CN), 162 MHz: 52.0, s.

X-ray crystallography

X-ray crystal structures of $[\text{Mo}(\text{C}\equiv\text{C}\text{-}\text{C}\equiv\text{CSiMe}_3)(\text{bipy})(\eta\text{-C}_7\text{H}_7)][\text{PF}_6]$, $[\mathbf{1}]\text{PF}_6$ and $[\{\text{Mo}(\text{dppe})(\eta\text{-C}_7\text{H}_7)\}_2\{\mu\text{-C}=\text{C}(\text{C}\equiv\text{CSiMe}_3)\text{C}(\text{C}\equiv\text{CSiMe}_3)=\text{C}\}][\text{PF}_6]_2\cdot 2.5\text{NCMe}$, $[\mathbf{3}][\text{PF}_6]_2\cdot 2.5\text{NCMe}$.

Single crystals of $[\mathbf{1}]\text{PF}_6$ were obtained as dark red plates by vapour diffusion of diethylether into an acetone solution of the complex and a crystal of dimensions 0.20 x 0.10 x 0.05 mm was selected for analysis. Single crystals of $[\mathbf{3}][\text{PF}_6]_2\cdot 2.5\text{NCMe}$ were obtained as brown-purple plates by vapour diffusion of diethylether into a NCMe solution of the complex and a crystal of dimensions 0.40 x 0.20 x 0.10 mm was selected for analysis. For both complexes, data collection, cell refinement and data reduction were carried out with Bruker SMART and Bruker SAINT software; SHELXS-97,¹ was employed for the computing structure solution and SHELXL-97,² for the computing structure refinement. Both structures were solved by direct methods with refinement based on F^2 . The asymmetric unit of $[\mathbf{3}]\text{PF}_6$ contains 2.5 molecules of solvent NCMe, some at partial occupancy, in the asymmetric unit. Additionally three of the Ph groups, both SiMe_3 groups and the PF_6 counter ions exhibited some disorder.

1. Sheldrick, G.M. SHELXS-97, Program for Crystal Structure Solution, Universität Göttingen, Germany, 1997.
2. Sheldrick, G.M. SHELXL-97, Program for Crystal Structure Refinement, Universität Göttingen, Germany, 1997.