Metal-stabilised diynyl radicals: structure and reactivity of [Mo(C≡C-C≡CSiMe3)L₂(η-C₇H₇)]⁺, (L₂ = 2,2'-bipyridine or dppe).


ELECTRONIC SUPPLEMENTARY INFORMATION

Preparations

Synthesis of [Mo(C≡C-C≡CSiMe3)(bipy)(η-C₇H₇)][PF₆], [1]PF₆

A purple solution of [Mo(C≡C-C≡CSiMe₃)(bipy)(η-C₇H₇)], 1, (0.494 g, 1.06 mmol) in dichloromethane (20 cm³) was cooled to −40°C and treated with [FeCp₂][PF₆] (0.352 g, 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 10 cm³) and then recrystallised from CH₂Cl₂/ diethylether. Yield 0.384 g, (59% based on 1).

Synthesis of [{Mo(dppe)(η-C₇H₇)}₂{μ-C=C(C≡CSiMe₃)C(C≡CSiMe₃)=C}][PF₆]₂, [3][PF₆]₂

A green solution of [Mo(C≡C-C≡CSiMe₃)(dppe)(η-C₇H₇)], 2a, (0.402 g, 0.57 mmol) in dichloromethane (30 cm³) was treated with [FeCp₂][PF₆] (0.233 g, 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 10 cm³) and then recrystallised from CH₂Cl₂/ diethylether. Yield 0.415 g, (85% based on 2a).

Spectroscopic and Analytical data

[Mo(C≡C-C≡CSiMe₃)(bipy)(η-C₇H₇)][PF₆], [1]PF₆

IR spectrum (CH₂Cl₂), ν(C≡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, [Mo(C≡C-C≡CSiMe₃)(Bu'bipy)(η-C₇H₇)][PF₆] (Bu'bipy = 4,4'-Bu₂-2,2'-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 (CH₂Cl₂), ν(C≡C), cm⁻¹: 2120.
Accurate mass, mass spectroscopy: C₈₀H₈₀Mo₂P₄Si₂ (+2) requires 707.1438; found 707.1442. C₈₀H₈₀Mo₂P₄Si₂PF₆ (+1) requires 1559.2600; found 1559.2559.
Microanalysis: C₈₀H₈₀Mo₂P₄Si₂PF₆ (+1) requires: C, 56.4%, H, 4.7%. Found: C, 55.6%, H, 4.5%.

¹H NMR (CD₂Cl₂) 300 MHz: 7.75-7.03, m, 40H, Ph(dppe); 4.82, s, 14H, C≡C; 2.91, br, 8H, CH₂ (dppe); 0.00, s, 18H, SiMe₃.

¹³C NMR (CD₂Cl₂), 100 MHz: 374.8, t, J(P-C) 30Hz, Mo≡C; 137.6-125.4, 105.3, Ph (dppe) and Cβ-Cδ, Mo≡C-C≡C≡SiMe₃; 93.9, C≡C; 29.0, CH₂ (dppe); −0.3, SiMe₃.

³¹P NMR (CD₃CN), 162 MHz: 52.0, s.

X-ray crystallography

X-ray crystal structures of [Mo(C≡C≡CSiMe₃)(bipy)(η-C₇H₇)][PF₆], [1]PF₆ and [{Mo(dppe)(η-C₇H₇)}₂{μ-C≡C≡CSiMe₃}C≡CSiMe₃≡C] [PF₆]₂.2.5NCMe, [3][PF₆]₂.2.5NCMe.

Single crystals of [1]PF₆ 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 mm was selected for analysis. Single crystals of [3][PF₆]₂.2.5NCMe 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 F². The asymmetric unit of [3]PF₆ contains 2.5 molecules of solvent NCMe, some at partial occupancy, in the asymmetric unit. Additionally three of the Ph groups, both SiMe₃ groups and the PF₆ counter ions exhibited some disorder.