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Comparative reactivity study of cyclopentadienyl and fulvalene molybdenum complexes

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Abstract

The reactions of $cis-1,1'-[\eta^5:\eta^5-(C_5H_3CO_2Me)_2]Mo_2(CO)_6$ (1), in the presence of 1 equiv. of Me₃NO, and $[(\eta^5-C_5H_4CO_2Me)Mo(CO)_3]_2$ (2) with dppe produce CO labilization and formation of the dinuclear zwitterions $trans-1,1'-[\eta^5:\eta^5-(C_5H_3CO_2Me)_2]Mo_2(CO)_5(dppe)$ (3) and disproportionation species $[(\eta^5-C_5H_4CO_2Me)Mo(CO)_2(dppe)]^+$ $[(\eta^5-C_5H_4CO_2Me)-Mo(CO)_3]^-$ (4), respectively. Using the same method, the reactions of $trans-1,1'-[\eta^5:\eta^5-(C_5H_3CO_2Me)_2]Mo_2(CO)_6I_2$ and $(\eta^5-C_5H_4CO_2Me)Mo(CO)_3I$ with PPh₃ in the presence of 1 and 2 equiv. of Me₃NO yield $trans-1,1'-[\eta^5:\eta^5-(C_5H_3CO_2Me)_2]-Mo_2(CO)_4(PPh_3)_2I_2$ (5) and $(\eta^5-C_5H_4CO_2Me)Mo(CO)_2(PPh_3)I$ (6). The reactions of the several anionic carbonyl species { $trans-1,1'-[\eta^5:\eta^5-(C_5H_3CO_2Me)_2]Mo_2(CO)_6\}^2^-$, $[(\eta^5:\eta^5-C_{10}H_8)W_2(CO)_6]^2^-$ and $[(\eta^5-C_5H_4CO_2Me)Mo(CO)_3]^-$ with S_2Ph_2 give rise to the thiolate–fulvalene complexes $cis-1,1'-[\eta^5:\eta^5-(C_5H_3CO_2Me)_2]Mo_2(CO)_4(\mu-SPh)_2$ (7) and $(\eta^5:\eta^5-C_{10}H_8)W_2(CO)_6(SPh)_2$ (8) and the thiolate–bridged dimer $[(\eta^5-C_5H_4CO_2Me)Mo(CO)(\mu-SPh)]_2$ (9). Treatment of 6 with 1 equiv. of HC=C-C=CH and with $(\eta^5-C_5H_4CO_2Me)Mo(CO)_2(PPh_3)(C=C-C=CH)$, in the presence of CuI at room temperature, afford the cyclopentadiene complexes $(\eta^5-C_5H_4CO_2Me)Mo(CO)_2(PPh_3)(C=C-C=CH)$ (10) and $(\eta^5-C_5H_4CO_2Me)(PPh_3)(CO)_2Mo-(C=C-C=C)-Mo(CO)(dppe)(\eta^5-C_5H_5)Mo(CO)(dppe)((-E-C=C=CH))$ with $Co_2(CO)_8$ yields $[Co_2\{\mu-HC_2C=C[Mo(CO)(dppe)-(\eta^5-C_5H_5)]Mo(CO)(dppe)(C=C-C=CH)$ with $Co_2(CO)_8$ yields $[Co_2\{\mu-HC_2C=C[Mo(CO)(dppe)-(\eta^5-C_5H_5)]Mo(CO)(dppe)-(\eta^5-C_5H_5)]Mo(CO)(dppe)-(\eta^5-C_5H_5)Mo(CO)(dppe)-(\eta^5-C_5H_5)Mo(CO)(dppe)-(\eta^5-C_5H_5)Mo(CO)(dppe)-(\eta^5-C_5H_5)Mo(CO)(dppe)-(\eta^5-C_5H_5)Mo(CO)(dppe)-(\eta^5-C_5H_5)Mo(CO)(dppe)-(\eta^5-C_5H_5)Mo(CO)(dppe)-(\eta^5-C_5H_5)Mo(CO)(dppe)-(\eta^5-C_5H_5)Mo(CO)(dppe)-(\eta^5-C_5H_5)Mo(CO)(dppe)-(\eta^5-C_5H_5)Mo(CO)(dppe)-(\eta^5-C_5H_5)Mo(CO)(dppe)-(\eta^5-C_5H_5)Mo(CO)(dppe)-(\eta^5-C_5H_5)Mo(CO)(dppe)-(\eta^5-C_5H_5)Mo(CO)(dppe)-$

Keywords: Fulvalene complexes; Cyclopentadiene complexes; Acetylene complexes; Molybdenum complexes

1. Introduction

Bimetallic fulvalene complexes have centered special attention over the last few decades [1–6]. The chemical behaviour of fulvalene carbonyl metal complexes is expected to differ from that of their cyclopentadienyl metal mononuclear and dimer analogues for several reasons. One of these reasons is due, in part, to the ability of the fulvalene ligand to allow for metal–metal bond cleavage while inhibiting fragmentation to mononuclear complexes; the potential for metal–metal cooperativity is maintained through relative proximity and possibly by communication through the π -bond system of the fulvalene [7]. Although transition-metal fulvalenyl complexes have been synthetized with many

metals, few comparative studies are found on related fulvalene and cyclopentadienyl complexes [8]. While phosphine-substituted cyclopentadienyltungsten or molybdenum carbonyl halocompounds $(\eta^5-C_5H_5)M_5$ (CO)₂LI and phosphine-substituted fulvalenedimolybdenum carbonyl dihalocompounds $(\eta^5:\eta^5-C_{10}H_8)$ - $Mo_2(CO)_4L_2I_2$ (L = PPh₃, PCy₃ and PXy₃) were readily prepared by direct thermal substituton of a CO ligand [9], the phosphine-substituted fulvalene-ditungsten carbonyl dihalocompounds can only be prepared under mild conditions by a new general procedure of synthesis using Me₃NO to remove one CO molecule at each metal center of the dihalide complexes [8a]. Whereas the reactions of molybdenum and tungsten cyclopentadienyl carbonyl complexes with thiolate (RS⁻) ligands form a well-defined subset among organometallic compounds [10,11], and are primarily of two general types with formulas $(\eta^{5}-C_{5}H_{5})M(CO)_{3}(SR)$, $[(\eta^{5}-C_{5}H_{5}) M(CO)_{2}(\mu-SR)_{2}$ (M = Mo, W) and $[(\eta^{5}-C_{5}H_{5})Mo-$

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 $(CO)(\mu$ -SR)]₂ [10], the reactivity of fulvalene metal complexes, in our knowledge, has been poorly studied [10f]. On the other hand, complexes in which sp carbon chains span transition metal end-groups are attracting increasing attention [12-15]. These wire like, unsaturated linear assemblies offer aesthetic appeal, a variety of interesting fundamental properties, and intriguing possibilities for molecular-level devices [16]. Specific properties of transition metal complexes result primarily from the ability of the metal to participate in π -delocalization, as well as the potential for interaction of the transition metal d-orbitals with the conjugated π -orbitals of the unsaturated carbon chains [17–20]. In order to make a comparative study between fulvalene and cyclopentadienyl complexes, in this paper we report the reactions of $[\eta^5:\eta^5-(C_5H_3CO_2Me)_2]Mo_2(CO)_6$ (1) and $[(\eta^5-C_5H_4CO_2Me)Mo(CO)_3]_2$ (2) with dppe and thiolate ligands as Ph_2S_2 and the synthesis of σ - and π -acetylene organometallic complexes.

2. Experimental

2.1. Reagents and general techniques

All manipulations were carried out by using standard Schlenk vacuum-line and syringe techniques under an atmosphere of oxygen-free Ar. All solvents for synthetic use were reagent grade. Diethyl ether, hexane, 1,2-DME and tetrahydrofurane (THF) were dried and distilled over sodium in the presence of benzophenone under an Ar atmosphere. Methanol was stored over molecular sieves (4 Å) under Ar. The solvents were bubbled with Ar for 1 h after distillation or degassed by means of at least three freeze-pump-thaw cycles after distillation and before use. Column chromatography was performed by using Alfa neutral alumina at activity II. Mo(CO)₆, W(CO)₆, Co₂(CO)₈, NaH, 1,2-bis-(diphenylphosphino)ethane (dppe), I₂, dimethylcarbon-(CH₃O–CO–OCH₃), S₂Ph₂, Et₂NH, DMSO, ate $Fe_2(SO_4)_3(H_2O)_n$, Na_2SO_4 anhydrous, $Na_2S_2O_3 \times 5H_2O$, KOH and glacial acetic acid (Fluka) and a solution 1.5 M of LiMe-LiBr in THF, PPh₃, CuI, 1,4-dicloro-2-butyne (ClCH₂C=CCH₂Cl), TMSA (Me₃SiC=CH) and a solution 1 M of LiEt₃BH in THF (Aldrich) were used as received. Me₃NO was sublimed prior to use and under argon. The compounds [ŋ⁵:ŋ⁵stored $(C_5H_3CO_2Me)_2$]Mo₂(CO)₆ (1) [21], [(η^5 -C₅H₄CO₂Me)-(2) [22], $\text{Li}_{2}\{[\eta^{5}:\eta^{5}-(C_{5}H_{3}CO_{2}Me)_{2}] Mo(CO)_3]_2$ $Mo_2(CO)_6$ } [21], $Li_2[(\eta^5:\eta^5-C_{10}H_8)W_2(CO)_6]$ [23], $(\eta^5-W_1)W_2(CO)_6$] [23], $(\eta^5-W_1)W_2(CO)_6$] $C_5H_4CO_2Me)Mo(CO)_3I$ [22], $[\eta^5:\eta^5-(C_5H_3CO_2Me)_2]$ - $Mo_2(CO)_6I_2$ [8c], and $(\eta^5-C_5H_5)Mo(CO)(dppe)(C \equiv$ $C-C \equiv CH$ [24] were prepared according to literature procedures and were purified by TLC. The ¹H-, ¹³C-, and ³¹P-NMR spectra were recorded on a Bruker AMX-300 and 500 instrument. Chemical shifts were

measured relative either to an internal reference of tetramethylsilane or to residual protons of the solvents. Infrared spectra were measured on a Perkin–Elmer 1650 infrared spectrometer. Elemental analyses were performed by the Mycroanalytical Laboratory of the University Autónoma of Madrid on a Perkin–Elmer 240 B microanalyser. Electronic spectra were recorded on a Pye Unicam SP 8-100 UV-Vis spectrophotometer. Mass spectra were measured on a VG-Autospec mass spectrometer for FAB or AIE by the Mass Laboratory of the University Autónoma of Madrid.

2.2. Synthesis of trans-1,1'- $[\eta^{5}:\eta^{5}-(C_{5}H_{3}CO_{2}Me)_{2}]Mo_{2}(CO)_{5}(dppe)$ (3)

Using the new general method for the synthesis of $[\eta^5:\eta^5-(C_5H_3CO_2Me)_2]Mo_2(CO)_5L_2$ [8c], trimethylamine N-oxide is used to chemically oxidize and remove one CO molecule. A solution of 0.20 g (0.32 mmol) of $[\eta^{5}:\eta^{5}-(C_{5}H_{3}CO_{2}Me)_{2}]Mo_{2}(CO)_{6}$ (1) (*cis* isomer) and 0.13 g (0.32 mmol) of dppe in 25 ml of THF was prepared. Trimethylamine N-oxide 0.036 g (0.32 mmol) was added with vigorous magnetic stirring. The solution was stirred until the reaction was seen to be completed by IR spectroscopy. After 10 min, no starting material remained. Solvent removal followed by recrystallization (CH₂Cl₂-hexane at -20° C) afforded 0.30 g of orange-brown crystalline product (95% yield). IR (THF, cm⁻¹): v_{CO} 1966 (vs), 1906 (s), 1801 (s), 1725 (CO₂Me). ¹H NMR (CD₂Cl₂, ppm) δ : 7.68 (m, o-H, 8H, Ph); 7.60 (m, m-H, 8H, Ph); 7.46 (m, p-H, 4H, Ph); 5.61 (m, 1H, Fv); 5.47 (m, 2H, Fv); 5.14 (m, 1H, Fv); 5.02 (m, 1H, Fv); 4.30 (m, 1H, Fv); 3.60 (s, 3H, CO₂CH₃); 3.48 (s, 3H, CO₂CH₃); 3.33 (d, 2H, -CH₂-); 1.67 (m, 2H, -CH₂-). ³¹P NMR (CD₂Cl₂, ppm) δ: 33.71 (s, 2P). Anal. Calc. for C₄₅H₃₆Mo₂O₉P₂: C, 55.44; H, 3.70. Found: C, 55.40; H, 3.66%.

2.3. Synthesis of $[(\eta^{5}-C_{5}H_{4}CO_{2}Me)Mo(CO)_{2}(dppe)]^{+}$ $[(\eta^{5}-C_{5}H_{4}CO_{2}Me)Mo(CO)_{3}]^{-}$ (4)

To a solution of 0.35 g (0.6 mmol) of $[(\eta^5 C_5H_4CO_2Me)Mo(CO)_{3]_2}$ (2) in THF (25 ml) was added 0.23 g (0.6 mmol) of dppe. The solution was stirred until the reaction was seen to be completed by IR spectroscopy (≈ 2 h). The volatiles were removed by vacuum and the residue, which was washed with hexane and dried in vacuo, afforded 0.53 g of a brown solid (90% yield). IR (THF, cm⁻¹): v_{CO} 1984 (vs), 1924 (m), 1906 (s), 1784 (s), 1734 (CO₂Me), 1713 (CO₂Me). ¹H NMR (CDCl₃, ppm) δ: 7.70 (m, *o*-H, 8H, Ph); 7.45 (m, *m*-H, 8H, Ph); 7.30 (m, *p*-H, 4H, Ph); 6.25 (t, $J_{HP} =$ 2.50 Hz, 2H, Cp); 5.95 (t, $J_{\rm HP} = 2.50$ Hz, 2H, Cp); 3.68 (s, 3H, CO₂CH₃); 3.31 (dd, 4H, -CH₂CH₂-). ³¹P NMR (CDCl₃, ppm) δ : 33.04 (s, 2P). Anal. Calc. for C₄₅H₃₈Mo₂O₉P₂: C, 55.33; H, 3.90. Found: C, 55.30; H, 3.85%.

2.4. Synthesis of trans-1,1'- $[\eta^5:\eta^5-(C_5H_3CO_2Me)_2]$ - $Mo_2(CO)_4(PPh_3)_2I_2$ (5)

A solution of *trans*-1,1'- $[\eta^5:\eta^5-(C_5H_3CO_2Me)_2]$ -Mo₂(CO)₆I₂ (0.34 g, 0.40 mmol) and 0.21 g (0.80 mmol) of PPh₃ in 30 ml of THF was prepared. Me₃NO (0.09 g, 0.80 mmol) was added with vigorous magnetic stirring. After 10 min, no starting material remained; the reddish-brown solid was extracted with CH₂Cl₂ and purified by TLC using CH₂Cl₂-hexane (1:2) as eluent. Solvent removal followed by recrystallization (CH₂Cl₂hexane, at -20° C) afforded red-brown crystalline product (0.47 g, 90% yield). IR (THF, cm⁻¹): v_{CO} 1974 (vs), 1897 (s), 1725 (CO₂Me). ¹H NMR (CDCl₃, ppm) δ : 7.67–7.40 (m, all Ph); *cis*–*cis* (*meso*) isomer (27%) δ : 6.47 (dd, 2H, Fv); 5.47 (dd, 2H, Fv); 4.75 (dd, 2H, Fv); 3.59 (s, 6H, CO₂CH₃); *cis*-*cis* (*dl*) isomer (34%) δ : 6.41 (dd, 1H, Fv); 6.21 (dd, 1H, Fv); 6.10 (dd, 1H, Fv); 5.70 (dd, 1H, Fv); 5.15 (dd, 1H, Fv); 4.15 (dd, 1H, Fv); 3.64 (s, 3H, CO₂CH₃); 3.55 (s, 3H, CO₂CH₃); cis-trans isomer (32%) δ : 6.30 (dd, 1H, Fv); 5.56 (dd, 1H, Fv); 5.42 (dd, 1H, Fv); 5.02 (dd, 1H, Fv); 4.92 (dd, 1H, Fv); 4.86 (dd, 1H, Fv); 3.72 (s, 3H, CO₂CH₃); 3.66 (s, 3H, CO₂CH₃); trans-trans isomer (7%) δ : 5.31 (dd, 2H, Fv); 4.80 (dd, 2H, Fv); 4.15 (dd, 2H, Fv); 3.79 (s, 6H, CO₂CH₃). ³¹P NMR (CDCl₃, ppm) *cis-cis* (*meso*) isomer δ : 43.68 (s, 2P); *cis*-*cis* (*dl*) isomer δ : 43.36 (s, 1P); 43.11 (s, 1P); *cis*-*trans* isomer δ : 44.37 (s, 1P); 62.94 (s, 1P); trans-trans isomer δ : 62.78 (s, 2P). MS: m/e: 1049.0 (M^+ -2I-CO). Anal. Calc. for C₅₄H₄₂I₂Mo₂-O₈P₂: C, 48.50; H, 3.14. Found: C, 48.57; H, 3.19%.

2.5. Synthesis of $(\eta^{5}-C_{5}H_{4}CO_{2}Me)Mo(CO)_{2}(PPh_{3})I$ (6)

The same procedure as described above was followed in the preparation of this compound, using 1.77 g (2.07 mmol) of $(\eta^{5}-C_{5}H_{4}CO_{2}Me)Mo(CO)_{3}I$, 0.54 g (2.07 mmol) of PPh₃ and 0.23 g (2.07 mmol) of Me₃NO. After 10 min the solvent was removed under vacuum and the product was purified by TLC using CH₂Cl₂hexane (1:2) as eluent. A red-brown residue was obtained (0.89 g, 65% yield). IR (THF, cm⁻¹): v_{CO} 1975 (vs), 1899 (s), 1726 (CO₂Me). ¹H NMR (CDCl₃, ppm) δ : 7.68–7.40 (m, all Ph); *cis* isomer (72%) δ : 6.11 (ddd, $J_{\rm HP} = 1.43, 1.43, 3.15$ Hz, 1H, Cp); 5.56 (ddd, $J_{\rm HP} =$ 1.43, 1.43, 3.15 Hz, 1H, Cp); 5.37 (ddd, $J_{\rm HP} = 1.43$, 1.43, 3.15 Hz, 1H, Cp); 5.28 (ddd, $J_{\rm HP} = 1.43$, 1.43, 3.15 Hz, 1H, Cp); 3.87 (s, 3H, CO₂CH₃); trans isomer (28%) δ : 5.42 (dt, $J_{\rm HP} = 2.36$, 2.36, 2H, Cp); 4.83 (dt, $J_{\rm HP} =$ 2.36, 2.36 Hz, 2H, Cp); 3.72 (s, 3H, CO₂CH₃). ¹³C NMR (CDCl₃, ppm) δ : 134.3–128.7 (Ph); *cis* isomer δ : 102.8 (s, C_i, Cp); 96.2 (s, C_o, Cp); 92.8 (s, C_m, Cp); 52.5 (s, Me, CO₂Me); *trans* isomer δ : 99.3 (s, C_i, Cp); 95.7 (s, C_o , Cp); 89.9 (s, C_m , Cp); 52.4 (s, Me, CO_2Me). ³¹P NMR (CDCl₃, ppm) *cis* isomer δ : 43.15 (s, 1P); *trans* isomer δ : 62.78 (s, 1P). MS: m/e: 638.0 (M^+ – CO).

Anal. Calc. for $C_{27}H_{22}IMoO_4P$: C, 48.80; H, 3.31. Found: C, 48.72; H, 3.26%.

2.6. Synthesis of cis-1,1'- $[\eta^{5}:\eta^{5}-(C_{5}H_{3}CO_{2}Me)_{2}]$ -Mo₂(CO)₄(μ -SPh)₂ (7)

A solution of S_2Ph_2 (0.42 g, 1.91 mmol) in THF (20 ml) was added to a solution of Li₂{trans-1,1'- $[\eta^5:\eta^5-$ (C₅H₃CO₂Me)₂]Mo₂(CO)₆} (0.95 mmol), prepared in situ from LiEt₃BH and cis-1,1'-[ŋ⁵:ŋ⁵-(C₅H₃CO₂- $Me_{2}Mo_{2}(CO)_{6}$ (1), in the same solvent (40 ml). During the addition period, the solution gradually changed from yellow to brown. Progress of the reaction was monitored periodically by infrared spectroscopy; after 5 min, a new band at 1858 cm⁻¹ attributed to cis-1,1'- $[\eta^{5}:\eta^{5}-(C_{5}H_{3}CO_{2}Me)_{2}]Mo_{2}(CO)_{4}(\mu-SPh)_{2}$ (7) was observed. After 2 h neither starting nor intermediate materials remained. Upon filtration and removal of the solvent under reduced pressure, a green-brown solid was obtained which was washed with hexane (0.49 g, 68% yield). IR (THF, cm⁻¹): v_{CO} 1960 (vs), 1858 (vs), 1739 (CO₂Me). ¹H NMR (CDCl₃, ppm) δ : 7.51 (m, o-H, 4H, Ph); 7.30 (m, m-H and p-Ph, 6H, Ph); 5.43 (m, 2H, Fv); 5.37 (m, 2H, Fv); 5.23 (m, 2H, Fv); 3.39 (s, 6H, CO₂CH₃). UV (THF): λ_{max} 416 nm. MS: m/e: 765.4 (M^+) , 713.3 $(M^+ - 2CO)$. Anal. Calc. for C₃₀H₂₂Mo₂O₉S₂: C, 27.91; H, 1.63. Found: C, 27.97; H, 1.67%.

2.7. Synthesis of $(\eta^{5}:\eta^{5}-C_{10}H_{8})W_{2}(CO)_{6}(SPh)_{2}$ (8)

This compound was prepared as described above using $Li_2[(\eta^5:\eta^5-C_{10}H_8)W_2(CO)_6]$ (0.21 g, 0.31 mmol) and S_2Ph_2 (0.14 g, 0.62 mmol). After 3 h the solution had changed from yellow to orange and the IR spectrum showed the total disappearance of the 1892 and 1800 cm⁻¹ peaks corresponding to the lithium salt and the appearance of two v_{CO} bands at 2023 and 1937 cm⁻¹ of the final product. Upon filtration and removal of the solvent under reduced pressure, a dark orange solid was obtained which was washed with hexane (0.22 g, 82% yield). IR (THF, cm⁻¹): v_{CO} 2023 (s), 1937 (vs). ¹H NMR (acetone-d₆, ppm) δ : 7.52 (m, *o*-H, 4H, Ph); 7.37 (m, m-H, 4H, Ph); 7.30 (m, p-H, 2H, Ph); 6.40 (t, 4H, Fv); 5.87 (t, 4H, Fv). Anal. Calc. for C₂₈H₁₈O₆S₂W₂: C, 38.19; H, 2.05. Found: C, 38.14; H, 2.15%.

2.8. Synthesis of $[(\eta^{5}-C_{5}H_{4}CO_{2}Me)Mo(CO)(\mu-SPh)]_{2}$ (9)

This complex was prepared in the same manner, using Li[$(\eta^5-C_5H_4CO_2Me)Mo(CO)_3$] (0.27 g, 0.87 mmol) and S₂Ph₂ (0.19 g, 0.87 mmol). The colour of the solution immediately turned from yellow to dark red. After 30 min neither starting nor intermediate materials remained. Upon filtration and removal of the solvent under reduce pressure a red-brown solid was obtained which was washed with hexane (0.47 g, 76%). IR (THF, cm⁻¹): v_{CO} 1926 (vs), 1833 (s). ¹H NMR (acetone-d₆, ppm) δ : 7.03 (m, *o*-H, 4H, Ph); 6.95 (m, *m*-H, 4H, Ph); 6.79 (m, *p*-H, 2H, Ph); *cis* isomer δ : 5.45 (dd, $J_{HS} =$ 2.15 Hz, 4H, Cp); 5.06 (m, 4H, Cp); 3.57 (s, 6H, CO₂CH₃); *trans* isomer δ : 5.06 (m, 2H, Cp); 4.98 (dd, $J_{HS} =$ 2.30 Hz, 2H, Cp); 4.82 (m, 2H, Cp); 4.78 (m, 2H, Cp); 3.55 (s, 6H, CO₂CH₃). UV (THF): λ_{max} 519, 342 nm. MS: m/e: 437.2 ($M^+ -$ 2CO - 2SPh). *Anal.* Calc. for C₂₈H₂₄Mo₂O₆S₂: C, 47.20; H, 3.37. Found: C, 46.96; H, 3.31%.

2.9. Synthesis of $(\eta^{5}-C_{5}H_{4}CO_{2}Me)Mo(CO)_{2}(PPh_{3})(C=C-C=CH)$ (10)

A solution of complex 6 (1.24 g, 1.87 mmol) in THF (10 ml) and Et_2NH (25 ml) was treated at $-80^{\circ}C$ with CuI (0.04 g, 0.217 mmol) and a solution of HC=C-C=CH (approximately 0.037 mol) in THF (25 ml) prepared in situ from ClCH₂C=CCH₂Cl and KOH at -80° C [25]. The reaction mixture was gradually warmed to room temperature (r.t.) and a change of colour, from reddish to dark yellow, was observed. The reaction was monitored by IR spectroscopy. Upon removal of the solvent under reduced pressure, a brown solid was obtained, and the product was extracted with hexane (0.80 g, 73% yield). IR (THF, cm⁻¹): $v_{C=C}$ 2158 (m), 2082 (w), 2054 (w); v_{CO} 1978 (s), 1903 (vs), 1726 (CO₂Me). ¹H NMR (CDCl₃, ppm) δ : 7.68–7.46 (m, all Ph); cis isomer (45%) δ : 6.11 (ddd, $J_{\text{HP}} = 1.43$, 1.43, 3.15 Hz, 1H, Cp); 5.56 (ddd, $J_{\rm HP} = 1.43$, 1.43, 3.15 Hz, 1H, Cp); 5.37 (ddd, $J_{\rm HP} = 1.43$, 1.43, 3.15 Hz, 1H, Cp); 5.28 (ddd, $J_{\rm HP} = 1.43$, 1.43, 3.15 Hz, 1H, Cp); 3.87 (s, 3H, CO₂CH₃); 2.09 (s, 1H, \equiv CH); *trans* isomer (55%) δ : 5.42 (dt, $J_{\rm HP} = 2.36$, 2.36, 2H, Cp); 4.83 (dt, $J_{\rm HP} = 2.36$, 2.36 Hz, 2H, Cp); 3.72 (s, 3H, CO₂CH₃); 2.04 (s, 1H, =CH). ¹³C NMR (CDCl₃, ppm) *trans* isomer δ : 188.7 (s, CO, CO₂Me); 134.9–128.7 (Ph); 125.4 (s, C_{α} , C=C-C=CH); 95.4 (s, C_i , Cp); 91.3 (s, C_o , Cp); 85.3 (s, C_m , Cp); 72.3 (s, C_β , C=C–C=CH); 70.9 (s, C_γ , C=C-C=CH); 60.9 (s, C_8 , C=C-C=CH); 45.2 (s, Me, CO₂Me). ³¹P NMR (CDCl₃, ppm) *cis* isomer δ : 43.88 (s, 1P); *trans* isomer δ : 63.52 (s, 1P). MS: m/e: 587.1 $(M^+);$ 534.9 $(M^+ - 2CO).$ Anal. Calc. for C₃₁H₂₃MoO₄P: C, 63.48; H, 3.92. Found: C, 63.54; H, 4.00%.

2.10. Synthesis of $Cp'(PPh_3)(CO)_2$ - $Mo-C \equiv C-C \equiv C-Mo(CO)(dppe)Cp$ (11) $[Cp' = (\eta^{5}-C_5H_4CO_2Me); Cp = (\eta^{5}-C_5H_5)]$

A solution of complex **6** (1.16 g, 1.75 mmol) in THF (10 ml) and Et₂NH (25 ml) was treated with CuI (0.039 g, 0.204 mmol) and 1.11 g (1.75 mmol) of (η^{5} -

 C_5H_5)Mo(CO)(dppe)(C=C-C=CH) [24]. The colour of the solution turned from reddish to dark orange. The solvent was removed under vacuum and the dark orange solid was purified by TLC using CH₂Cl₂-hexane (2:1) as eluent (1.60 g, 78% yield). IR (THF, cm^{-1}): v_{C=C} 2125 (vw), 2052 (w), v_{CO} 1978 (s), 1903 (vs), 1854 (vs); 1725 (CO₂Me). ¹H NMR (CDCl₃, ppm) δ : 7.50– 7.28 (m, all Ph); 4.51 (d, $J_{\rm HP} = 2.39$ Hz, 5H, Cp); 3.04 (m, 2H, -CH₂-); 1.67 (m, 2H, -CH₂-); cis isomer (34%) δ : 6.11 (ddd, $J_{\rm HP} = 1.45$, 1.45, 3.20 Hz, 1H, Cp'); 5.56 (ddd, $J_{\rm HP} = 1.45$, 1.45, 3.20 Hz, 1H, Cp'); 5.37 (ddd, $J_{\rm HP} = 1.45, 1.45, 3.20$ Hz, 1H, Cp'); 5.28 (ddd, $J_{\rm HP} =$ 1.45, 1.45, 3.20 Hz, 1H, Cp'); 3.87 (s, 3H, CO₂CH₃); *trans* isomer (66%) δ : 5.42 (dt, $J_{\rm HP} = 2.39$, 2.39 Hz, 2H, Cp'); 4.83 (dt, $J_{\rm HP} = 2.39$, 2.39 Hz, 2H, Cp'); 3.76 (s, 3H, CO₂CH₃). ¹³C NMR (CDCl₃, ppm) *trans* isomer δ : 134.5-128.6 (Ph); 106.8 (s, -C=C-C=C-); 101.7 (s, $-C \equiv C - C \equiv C -$; 99.3 (s, Cp); 95.6 (s, C_i, Cp'); 92.7 (s, $-C \equiv C - C \equiv C -$; 89.9 (s, C_o , Cp'); 87.6 (s, C_m , Cp'); 70.9 (s, $-C \equiv C - C \equiv C -$); 42.4 (s, Me, CO_2Me). ³¹P NMR (CDCl₃, ppm) δ : 93.29 (d, $J_{PP} = 37.06$ Hz, 1P, dppe); 61.94 (d, $J_{\rm PP} = 37.98$ Hz, 1P, dppe); *cis* isomer δ : 43.16 (s, 1P, PPh₃); trans isomer δ : 62.80 (s, 1P, PPh₃). MS: 1088.0 $(M^+ - 3CO).$ m/e: Anal. Calc. for C₆₃H₅₁Mo₂O₅P₃: C, 64.51; H, 4.35. Found: C, 64.56; H, 4.39%.

2.11. Synthesis of $[Co_2\{\mu-HC_2C \equiv C[Mo(CO)-(dppe)(\eta^5-C_5H_5)]\}(CO)_6]$ (12)

A solution of $(\eta^5-C_5H_5)Mo(CO)(dppe)(C=C-C=CH)$ [24] (0.12 g, 0.19 mmol) in hexane (20 ml) was treated with 0.06 g (0.19 mmol) of $Co_2(CO)_8$. After 3 h no starting material remained. Upon removal of the solvent under reduced pressure a reddish-brown solid was obtained, and the product was extracted with hexane and purified by TLC using hexane as eluent (0.13 g)75% yield). IR (CDCl₃, cm⁻¹): $v_{C=C}$ 2105 (w), v_{CO} 2082 (m); 2059 (vs); 2040 (s), 2027 (sh), 1866 (s). ¹H NMR (CDCl₃, ppm) δ: 7.73–7.31 (m, all Ph); 6.22 (s, 1H, =CH); 4.51 (d, J_{HP} = 2.32 Hz, 5H, Cp); 2.96 (dd, 4H, -CH₂CH₂-). ³¹P NMR (CDCl₃, ppm) δ : 92.75 (d, $J_{\rm PP} = 38.58$ Hz, 1P); 67.55 (d, $J_{\rm PP} = 38.62$ Hz, 1P). MS: $(M^+ - dppe)$. Anal. 524.2 m/e: Calc. for C₄₂H₃₀Co₂MoO₇P₂: C, 54.64; H, 3.25. Found: C, 54.60; H, 3.20%.

3. Results and discussion

3.1. Reactions of cis-1,1'- $[\eta^{5}:\eta^{5}-(C_{5}H_{3}CO_{2}Me)_{2}]Mo_{2}(CO)_{6}$ (1) and $[(\eta^{5}-C_{5}H_{4}CO_{2}Me)Mo(CO)_{3}]_{2}$ (2) with dppe

The reactions of $Cp_2Mo_2(CO)_6$ with PR_3 may yield phosphine-substituted Mo–Mo bonded dimers

 $Cp_2Mo_2(CO)_{6-x}(PR_3)_x$ (x = 1, 2) [26] or disproportionation products [CpMo(CO)₂(PR₃)₂]⁺ [CpMo(CO)₃]⁻ [27,28] depending on reaction conditions and the electronic and steric properties of PR₃. Disproportionation is favoured over phosphine-substituted dimers when electron-rich sterically undemanding and/or chelating phosphines are used. The preparation of zwitterionic fulvalene complexes are of interest in the context of nonlinear optics [29-32]. The reaction of $[\eta^5:\eta^5-$ (C₁₀H₈)]Mo₂(CO)₆ with PPh₃, Ph₂P-CH₂-PPh₂ or Ph₂P-CH₂CH₂-PPh₂ under thermal or photochemical conditions gave no isolable products. Recently, it has been shown that reactions of $[\eta^5:\eta^5-(C_5H_3CO_2Me)_2]$ - $Mo_2(CO)_6$ with PPhMe₂, PPh₂Me, P(n-Bu)₃ or PMe₃ in the presence of 1 equiv. of Me₃NO lead in high yield to the formation of yellow-brown analytically pure products of composition $[\eta^5:\eta^5-(C_5H_3CO_2Me)_2]Mo_2(CO)_5L_2$ [8c]. When we use P-donor ligands with cone angle $\theta \ge 145^{\circ}$ such as PPh₃ or PCy₃, the reactions gave no isolable products. Following a similar procedure, the reaction of $[\eta^5:\eta^5-(C_5H_3CO_2Me)_2]Mo_2(CO)_6$ (1) (cis isomer) with dppe in THF solution in the presence of 1 equiv. of Me₃NO lead to the formation of zwitterionic product of composition *trans*-1,1'- $[\eta^5:\eta^5 (C_5H_3CO_2Me)_2$]Mo₂(CO)₅(dppe) (3). This reaction does not take place thermally unless Me₃NO is present. The reaction of $[(\eta^5-C_5H_4CO_2Me)Mo(CO)_3]_2$ (2) with dppe leads to the formation of the disproportionation compound $[(\eta^5-C_5H_4CO_2Me)Mo(CO)_2(dppe)]^+$ [(n⁵- $C_5H_4CO_2Me)Mo(CO)_3$ ⁻ (4), and in this case, the presence of Me₃NO is not necessary. This different behaviour observed can be due to a stronger Mo-CO bond in the fulvalene complex 1 than cyclopentadienyl analogous compound 2. Both compounds are partially soluble in THF, CH₂Cl₂ and acetonitrile. IR monitoring of these reactions shows the formation of one isosbestic point at 2010 cm^{-1} which is indicative of a clean reaction without the formation of detectable intermediates and secondary products. The IR spectra of 3 and 4 show bands at 1906 (s), 1801 (s) cm^{-1} and 1906 (s), 1784 (s) cm^{-1} , respectively, due to the anionic fragment, and are very similar to those shown by the Li_{2} {*trans*-1,1'-[η^{5} : η^{5} -($C_{5}H_{3}CO_{2}Me$)₂]lithium salts $Mo_2(CO)_6$ [21] and $Li[(\eta^5-C_5H_4CO_2Me)Mo(CO)_3]$ [22] previously prepared. Bands at 1966 (vs) (3) and 1984 (vs), 1924 (m) (4) cm⁻¹, respectively, are assigned to the cationic fragment, by analogy to $[CpMo(CO)_2L_2]^+$ $(2000-1990 \text{ and } 1920-1900 \text{ cm}^{-1})$ [9a,26a,33]. For the compound **3** another band at ca. 1915 cm⁻¹, should be observed and is overlapped by the strong band at 1906 cm^{-1} of the anionic fragment. The intensity ratios are consistent with the cis geometry [34] (high-energy band more intense). Only cis isomers are also observed for the $FvMo_2(CO)_4L_2X_2$ (L = PPh₃, PCy₃, PXy₃; X = Cl, Br) [9b] and $[\eta^5:\eta^5-(C_5H_3CO_2Me)_2]Mo_2(CO)_5L_2$ (L = PPh_2Me , $PPhMe_2$, $P(n-Bu)_3$ [8c] compounds. The presence of five fulvalene resonances in the ¹H NMR spectra shows that 3 is less symmetrical than its substrates. Decoupling ${}^{1}H-{}^{1}H$ experiments show that only the signal of the broad multiplet at 5.47 ppm is coupled, so that it corresponds to two protons of the same ring. This experiment made possible the assignment of the two halves of the fulvalene systems. The signals at 5.61, 5.02 and 4.30 ppm are assigned to the cationic fragment and the signals at 5.47 and 5.14 ppm to the anionic half by analogy with the lithium salt previously prepared [21]. For the compound 4, only two signals at 6.25 and 5.95 ppm attributed to the cationic fragment are observed. The signals due to the anionic half could not be observed; the same happened in analogous compounds [33]. The ³¹P NMR spectra shows a single signal for both compounds at ca. 33.04 ppm in the characteristic range of the cis isomer [9b,35]. The zwitterionic character is also demostrated by the reaction between the anionic half of **3** and **4** with an electrophile as MeI to yield the methyl salts {*trans*-1,1'- $[\eta^5:\eta^5 (C_5H_3CO_2Me)_2$]Mo₂(CO)₅(dppe)(Me)}I and [(n⁵- $C_5H_4CO_2Me)Mo(CO)_3(Me)$ in addition to $[(\eta^5-C_5H_4CO_2Me)Mo(CO)_2(dppe)]^+I^-$ respectively, the salts could not be isolated, but were characterized by their IR spectra. During the reaction, the disappearance of the two bands due to the anionic half and the appearance of two new bands (2022, 1939 cm⁻¹) attributed to the methylated fragment is observed. The IR v_{CO} data for the reaction product shown that the CO stretching frequencies for the unreacted cationic half remained virtually unchanged.

3.2. Cyclopentadienyl and fulvalene thiolate complexes

The reaction of $\text{Li}[(\eta^5-C_5H_4CO_2Me)Mo(CO)_3]$ [22] with S₂Ph₂ in THF solution leads to the formation of brown compound $[(\eta^5-C_5H_4CO_2Me)Mo(CO)(\mu-SPh)]_2$ (9). This method involves nucleophilic displacement of the group -SPh in S_2Ph_2 using the anionic complex as nucleophile. The reaction was monitored by IR spectroscopy and when the reactants were mixed, carbonyl stretching frequencies due to starting material disappeared and four bands at 2029, 1976, 1944 and 1868 cm^{-1} were observed. The first and third absorptions correspond closely to values reported for monomeric $(\eta^{5}-C_{5}H_{5})M(CO)_{3}(SR)$ (M = Mo, W) species [10] and indicate the presence of $(\eta^5-C_5H_4CO_2Me)Mo$ -(CO)₃(SPh). The other two bands closely resemble those of $[(\eta^5-C_5H_5)M(CO)_2(\mu-SR)]_2$ species (M = Mo, W) [10] and are assigned to the dimeric $[(\eta^5 C_5H_4CO_2Me)Mo(CO)_2(\mu-SPh)]_2$ compound. After about 30 min these bands disappeared and two new bands at 1926 and 1833 cm⁻¹ were observed in the charactheristic range of $[(\eta^5-C_5H_5)M(CO)(\mu-SR)]_2$ (M = Mo, W) species [10b], which are assigned to the dimeric compound 9 with a formal double bond

Mo-Mo (Scheme 1). The presence of two v_{CO} bands may indicate that the compound can exist as a mixture of *cis* and *trans* isomers. In fact, the ¹H NMR spectrum shows six signals, because of the presence of non-equivalent Cp' ligands in the trans isomer, those at 5.45 and 5.06 ppm are attributed to eight protons of two cyclopentadienyl rings for the *cis* isomer and those at 5.06, 4.98, 4.82 and 4.78 ppm are due to eight protons of two cyclopentadienyl rings for the trans isomer. Two singlets at 3.57 and 3.55 ppm also appear, corresponding to the methyl protons of -CO₂Me groups in both isomers. The UV spectrum shows bands at 519 and 342 nm, which are attributed to the $d_{\pi} \rightarrow \sigma^*$ and $\sigma \rightarrow \sigma^*$ transitions, respectively. The last transition can be associated with the metal-metal bond [36]. The higher decarbonylation observed with respect the unsubstituted cyclopentadienyl PPN[$(\eta^5-C_5H_5)Mo(CO)_3$] compound, leads to the dimeric $[(\eta^5-C_5H_5)Mo(CO)_2 (\mu$ -SPh)]₂ specie [10a]. This can be due to negative inductive and mesomer effects of $-CO_2Me$ group in the cyclopentadienyl ring, which lead to a faster reaction rate. The reactions of fulvalene complexes Li₂{trans- $1,1'-[\eta^5:\eta^5-(C_5H_3CO_2Me)_2]Mo_2(CO)_6$ [21] and $Li_{2}[(\eta^{5}:\eta^{5}-C_{10}H_{8})W_{2}(CO)_{6}]$ [23] with S₂Ph₂ produce the cis-1,1'-[η⁵:η⁵-(C₅H₃CO₂Me)₂]Mo₂(CO)₄(µ-SPh)₂ (7) and $(\eta^{5}:\eta^{5}-C_{10}H_{8})W_{2}(CO)_{6}(SPh)_{2}$ (8) compounds respectively (Scheme 1). For the molybdenum fulvalene complex, IR monitoring shows at the begining of the reaction two v_{CO} bands at 2032 and 1951 cm⁻¹ due to the formation of the trans-1,1'- $[\eta^5:\eta^5-(C_5H_3CO_2Me)_2]$ - $Mo_2(CO)_6(SPh)_2$ compound. At the end of the reaction, only two new bands at 1960 and 1858 cm⁻¹ are observed, and are attributed to the compound 7. For the tungstene fulvalene complex, IR monitoring only shows



Scheme 1.

two new bands at 2023 and 1937 cm⁻¹ in the characteristic range of $(\eta^5-C_5H_5)M(CO)_3(SR)$ (M = Mo, W) complexes [10b] and the dark orange solid isolated was identified as 8. The ¹H NMR spectrum for 7 presents three multiplets at 5.43, 5.37 and 5.23 ppm due to six protons of the fulvalene ring, and a singlet at 3.39 ppm assigned to the methyl protons of the $-CO_2Me$ group. 8 shows two triplets at 6.40 and 5.87 ppm due to eight protons of the fulvalene ring; these values are similar to $(\eta^5:\eta^5-C_{10}H_8)W(CO)_6I_2$ compound [23] whose X-ray structure was determined and consists of two W(CO)₃I units which are at opposite sides of the fulvalene ligand [8a]. The different degree of decarbonylation observed between the cyclopentadienyl (9) and fulvalene (7) molybdenum complexes can be due to the difficulty in 7 to yield a double M=M bond, which would lead to the bending away from the planarity of the rings. The minor degree of decarbonylation of 8 with respect to 7 indicates the higher stability of thiolate tungsten species as compared to analogous molybdenum compounds. A

similar behaviour is observed in cyclopentadienyl complexes [10a].

3.3. Cyclopentadienyl and fulvalene butadiynyl complexes

The reaction of $(\eta^5 - C_5 H_4 CO_2 Me) Mo(CO)_3 I$ [22] with PPh₃ in the presence of 1 equiv. of Me₃NO gives the derivative $(\eta^5 - C_5 H_4 CO_2 Me) Mo$ monosubstituted $(CO)_3(PPh_3)I$ (6) in high yield as a mixture of *cis* and trans isomers (Scheme 2). The identity of the isomers was proven according to well-established IR and NMR criteria [34,35,37]. The ¹H-NMR spectrum shows six signals due to protons of the carbometoxycyclopentadienyl ring. According to δ values, integrals and bidimensional spectroscopy COSY (Fig. 1), the double doublet of doublets signals at 6.11, 5.56, 5.37 and 5.28 ppm $(J_{\rm HP} = 1.43, 1.43 \text{ and } 3.15 \text{ Hz}, \text{ respectively})$ are assigned to the cis isomer while the doublet of triplets signals at 5.42 and 4.83 ppm ($J_{\rm HP} = 2.36$ and 2.36 Hz, respec-



Fig. 1. COSY experiment for 6 in CDCl₃.









tively) are due to the *trans* isomer. The ³¹P NMR spectrum exhibits two singlets at 43.15 (*cis*) and 62.78 ppm (*trans*). The ratio of *cis:trans* isomers obtained from the integrals of these resonances (72:28) agreed reasonably well with that obtained from ¹H NMR data. The IR spectrum in THF exhibits two absorption

bands at 1975 (vs) and 1899 (s) cm⁻¹ associated with terminal v_{CO} modes. The higher frequency (sym) which is more intense than the lower one (antisym), supports the isomers ratio made from the ¹H and ³¹P NMR data. The air-unstable yellow diynyl complex (η^5 -C₅H₄-CO₂Me)Mo(CO)₃(PPh₃)(C=C-C=CH) (**10**) was ob-

tained from the CuI-catalyzed reaction between 6 and buta-1,3-diyne [25] in the presence of diethylamine and THF, which serves both to generate the active diynylcopper intermediate and to remove HCl as diethylammonium chloride (Scheme 2). The complex is characterized from its spectral properties and mass spectrum. The ¹H NMR spectrum shows the same six signals due to protons of the carbometoxycyclopentadienyl ring, and two new singlets resonances at 2.09 and 2.04 ppm assigned to the terminal =CH of the *cis* and trans isomers, respectively. Two signals at 43.88 (cis) and 63.52 (trans) ppm appear in the ³¹P NMR spectrum. The ratio of both isomers obtained from ¹H and ³¹P NMR data is 45:55. Using the same methodology, the homobimetallic $-C_4-$ ($\eta^5-C_5H_4CO_2Me$)(PPh₃)- $(CO)_2Mo-(C\equiv C-C\equiv C)-Mo(CO)(dppe)(\eta^5-C_5H_5)$ (11)complex was obtained by reaction between 6 and $(\eta^{5}-$ C₅H₅)Mo(CO)(dppe)(C=C-C=CH) [24] as a mixture of cis and trans isomers with respect to the PPh₃ ligand (Scheme 2). The IR spectrum in THF exhibits three v_{CO}



Fig. 2. Schematic representation of the four different stereoisomers of **5**.

absorptions at 1978 (s), 1903 (vs) and 1854 (vs) cm $^{-1}$ and two weak $v_{C=C}$ bands at 2125 and 2052 cm⁻¹. The ¹H NMR spectrum shows the signals due to Cp and Cp' proton rings for both isomers and in the ³¹P NMR spectrum at approximately 93 and 62 ppm two doblet signals are observed which are consistent with a cis arrangement of the dppe ligand. At approximately 43 (cis) and 62 (trans) ppm, the PPh₃ ligand signal appears. The ¹³C NMR data exhibits four resonances of the $-C_4$ chain at 106.8, 101.7, 92.7 and 70.9 ppm. $(\eta^{5}-C_{5}H_{5})Mo(CO)(dppe)$ -Reaction between (C=C-C=CH) [24] and Co₂(CO)₈ in hexane resulted in the mixed complex $[Co_2{\mu-HC_2C=C[Mo(CO)(dppe)(\eta^5 C_5H_5$](CO)₆] (12) (Scheme 2). The v_{CO} spectrum contained four absorptions; the characteristic pattern of a coordinated $Co_2(CO)_6$ unit (three bands) and a v_{CO} at 1866 cm⁻¹ due to the Mo fragment, which upon substitution was increased (1847 cm⁻¹ in the parent complex). For the preparation of butadiynyl fulvalene analogous complex, we previously isolated in high yield the trans-1,1'- $[\eta^5:\eta^5-(C_5H_3CO_2Me)_2]Mo_2(CO)_4(PPh_3)_2I_2$ (5) by reaction between the *trans*-1,1'- $[\eta^5:\eta^5-$ (C₅H₃CO₂Me)₂]Mo₂(CO)₆I₂ and PPh₃ in THF in the presence of 2 equiv. of Me₃NO (Scheme 3). The compound 5 may exist as four different geometrical isomers (not including enantiomers), trans-trans, cis-trans, cis-cis (meso) and cis-cis (dl) (Fig. 2). Two CO stretching vibrations at 1974 (vs) and 1897 (s) are observed. The intensity ratio is consistent with the basic cis geometry (the more intense the higher frequency). The ¹H NMR data for this complex is listed in the experimental section. The spectrum has been assigned on the basis of chemical shift, integrals, spin-spin coupling information, and two-dimensional homonuclear correlation spectroscopy (COSY and NOESY) [38]. The ¹H NMR spectrum can give rise to 18 signals due to fulvalene proton rings (three for each transtrans and cis-cis (meso) isomers and six for each cis-trans and cis-cis (dl) isomers) (Fig. 2). The trans half of cis-trans-5 is diastereotopic due to its chiral cis half and apparently is the only species in this system which exhibits a full ABX resonance pattern. The fulvalene region of the spectrum displays the expected signals relatively well resolved. According to COSY spectrum, including the normal (1D) spectrum for comparison of the diagonal connectivities, the protons corresponding to each of the fulvalene rings can be distinguished and assigned unambigously (Section 2). The ratio of trans-trans, cis-trans, cis-cis (meso) and cis-cis (dl) was found to be 7:32:27:34 on the basis of integrals. The ³¹P NMR spectrum exhibits six resonances at δ 62.7 (trans-trans), 62.9 (cis-trans), 44.4 (cis-trans), 43.7 (cis-cis (meso)), 43.3 and 43.1 (cis-cis (dl)), respectively. The cis:trans ratios found for the fulvalene dimolybdenum complex is similar to that for cyclopentadienyldimolybdenum analogous compound. The reaction of **5** with buta-1,3-diyne was carried out under similar conditions to those for the cyclopentadienyl analogous compound. A very air-unstable yellow solid was extracted with hexane but could not be characterized. The higher unstability for the butadiynyl fulvalene complex with respect to the butadiynyl cyclopentadienyl analogous compound **10** was observed.

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