

# Homo- and Heterobimetallic, Mixed Valence M<sup>II</sup>/M<sup>0</sup> Complexes of Molybdenum and Tungsten with S<sub>2</sub>CPR<sub>3</sub> Ligands. X-ray Structure of [( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)(CO)<sub>2</sub>Mo( $\mu$ -Br)( $\mu$ -S<sub>2</sub>CPCy<sub>3</sub>)Mo(CO)<sub>3</sub>]

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Addition of S<sub>2</sub>CPR<sub>3</sub> to [( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)M(CO)<sub>2</sub>(nitrile)<sub>2</sub>Br] (M = Mo, W) at room temperature readily produces mononuclear complexes [( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)M(CO)<sub>2</sub>(S<sub>2</sub>CPR<sub>3</sub>)Br] [R = Cy, Pr<sup>i</sup>] which have been isolated as crystalline solids and characterized by analytical and spectroscopic methods. These mononuclear complexes react with [M(CO)<sub>3</sub>(nitrile)<sub>3</sub>] (M = Mo, W), in CH<sub>2</sub>Cl<sub>2</sub> to afford dinuclear complexes of formula [( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)(CO)<sub>2</sub>M<sup>II</sup>( $\mu$ -Br)( $\mu$ -S<sub>2</sub>CPR<sub>3</sub>)M<sup>0</sup>(CO)<sub>3</sub>] (M<sup>II</sup> = Mo, 4a-d; M<sup>II</sup> = W, 5a-d). An X-ray determination of the derivative with M<sup>II</sup> = M<sup>0</sup> = Mo and R = Cy [4a, triclinic, space group P $\bar{1}$ , *a* = 10.037(5) Å, *b* = 10.669(5) Å, *c* = 15.323(6) Å,  $\alpha$  = 84.52(3)°,  $\beta$  = 78.40(3)°,  $\gamma$  = 82.01(4)°, *Z* = 2, *R* = 0.042, *R<sub>w</sub>* = 0.043] shows the presence of the S<sub>2</sub>CPCy<sub>3</sub> ligand coordinated as a  $\eta^2$ -S,S' chelate to Mo<sup>II</sup> and as a  $\eta^3$ -S,C,S' pseudoallyl to Mo<sup>0</sup>. The spectroscopic properties, particularly the signals of the central carbons of the S<sub>2</sub>CPR<sub>3</sub> bridge and of the allyl, together with the results of the X-ray structure determination of 4a, permit an unambiguous assignment of the structures of all the derivatives 4 and 5. For all combinations of metals (Mo<sup>II</sup>/Mo<sup>0</sup>, Mo<sup>II</sup>/W<sup>0</sup>, W<sup>II</sup>/Mo<sup>0</sup>, or W<sup>II</sup>/W<sup>0</sup>), a bond is formed selectively between the central carbon of S<sub>2</sub>CPR<sub>3</sub> and the metal atom in oxidation state zero.

## Introduction

The interesting reactivity patterns displayed by binuclear complexes of manganese containing S<sub>2</sub>CPR<sub>3</sub> bridges<sup>1,2</sup> in reactions of reduction and hydride addition<sup>3</sup> prompted us to undertake a systematic search for the rational synthesis of similar complexes of other metals. We have recently reported a high-yield procedure for the preparation of binuclear complexes containing S<sub>2</sub>CPR<sub>3</sub> bridging ligands acting as an  $\eta^2$ -S,S' chelate to manganese and as a  $\eta^3$ -S,C,S' pseudoallyl to molybdenum.<sup>4</sup> Similar methods lead to heterobinuclear complexes with other combinations of metals, such as Re/Mo<sup>5</sup> or Ru/W.<sup>6</sup> The procedure uses a mononuclear substrate which contains one terminal halide and one chelate S<sub>2</sub>CPR<sub>3</sub> attached to the same metal, as in [M(CO)<sub>3</sub>(S<sub>2</sub>CPR<sub>3</sub>)Br] (M = Mn,<sup>4</sup> or Re<sup>5</sup>) or in [Ru( $\eta^6$ -arene)(S<sub>2</sub>CPR<sub>3</sub>)Cl]PF<sub>6</sub>.<sup>6</sup> The reaction of such substrates with [M(CO)<sub>3</sub>(nitrile)<sub>3</sub>] (M = Mo, W) affords the desired binuclear complexes *via* the substitution of the nitrile ligands by the S,C,S',X set of atoms. In this way, the starting halogeno complex acts as a sort of multidentate ligand toward the {M(CO)<sub>3</sub>} fragment. In all the cases we

have studied previously, the reaction afforded selectively the product in which the central carbon of the S<sub>2</sub>CPR<sub>3</sub> ligand was bonded to the metal atom (Mo or W) of the fragment originated from the [M(CO)<sub>3</sub>(nitrile)<sub>3</sub>] complex. To account for this selectivity, we have advanced a tentative explanation based on the different oxidation numbers of the metals concerned.<sup>4</sup> In all the cases mentioned above, the compounds are heterobinuclear, and therefore, the central carbon of the  $\eta^3$ -S<sub>2</sub>CPR<sub>3</sub> ligand must choose between two different metals which, additionally, have different oxidation states. To test the validity of our explanation, we considered it of interest to attempt the preparation of binuclear complexes containing two atoms of the same metal with different oxidation states, thus ruling out the possible effects coming from the different natures of the metals involved. This study required the preparation of new mononuclear halogeno complexes of molybdenum and tungsten, to be used as substrates in the preparation of the binuclear compounds.

Apart from the heterobinuclear examples prepared by our group,<sup>4-7</sup> several mononuclear molybdenum complexes containing S<sub>2</sub>CPR<sub>3</sub> bonded as monodentate,<sup>8</sup> chelate,<sup>9</sup> or as  $\eta^3$ -S,C,S' pseudoallyl,<sup>10</sup> have been reported. [Mo(CO)<sub>2</sub>(PEt<sub>3</sub>)( $\mu$ -S<sub>2</sub>CPeEt<sub>3</sub>)<sub>2</sub>]<sub>2</sub><sup>8</sup> and [Mo<sub>2</sub>(S<sub>2</sub>CPeEt<sub>3</sub>)(O<sub>2</sub>CCH<sub>3</sub>)<sub>3</sub>(OPeEt<sub>3</sub>)]BF<sub>4</sub><sup>11</sup> are the only previously known dimolybdenum

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species with  $S_2CPR_3$  bridges which have been unambiguously characterized.

### Experimental Section

All reactions were carried out in dry solvents under a nitrogen atmosphere. Literature procedures for the preparation of starting materials are quoted in each case. Ligands and other reagents were purchased and used without purification unless otherwise stated.

**[Mo( $\eta^3-C_3H_5$ )(CO) $_2$ ( $S_2CPCy_3$ )Br] (2a).** A mixture of [Mo(CO) $_6$ ] (0.264 g, 1 mmol) and allyl bromide (100  $\mu$ L, 1.16 mmol), in acetonitrile (20 mL) was heated to reflux temperature for 3 h. After cooling to room temperature, the solvent was evaporated to afford [Mo( $\eta^3-C_3H_5$ )(CO) $_2$ (NCMe) $_2$ Br] $^{12}$  (ca. 1 mmol) as a yellow microcrystalline solid. This was dissolved in a mixture of  $CH_2Cl_2$  (10 mL) and  $CS_2$  (1 mL),  $S_2CPCy_3$  (0.357 g, 1 mmol) was added, and the mixture was stirred for 20 min at room temperature. After concentration in vacuo to half volume, addition of hexane (10 mL) and stirring for 5 min produced the precipitation of 2a as a greenish-blue solid which was recrystallized from  $CH_2Cl_2$ /hexane. Yield: 0.45 g, 72%. Anal. Calcd for  $C_{24}H_{38}BrMoO_2PS_2$ : C, 45.79; H, 6.08. Found: C, 46.03; H, 6.25.  $^1H$  NMR, ( $CD_2Cl_2$ ):  $\delta$  4.20 [m, 1H,  $C^2H$  of allyl], 3.57 [d (7), 2H,  $H$  syn of allyl], 2.65 [m, 3H,  $PC^1H$ ], 1.87–1.26 [m, 30H,  $CH_2$  of  $PCy_3$ ], 1.36 [d (10), 2H,  $H$  anti of allyl].

**[Mo( $\eta^3-C_3H_5$ )(CO) $_2$ ( $S_2CPPr_3$ )Br] (2b).** To a solution of [Mo( $\eta^3-C_3H_5$ )(CO) $_2$ (NCMe) $_2$ Br] (ca. 1 mmol) in  $CH_2Cl_2$  (20 mL), prepared as described above, was added  $CS_2$  (2 mL, excess), and then  $PPr_3$  (160  $\mu$ L, 1 mmol). The stirring time and workup were as described for compound 2a. Yield: 0.33 g, 65%. Anal. Calcd for  $C_{15}H_{26}BrMoO_2PS_2$ : C, 35.37; H, 5.14. Found: C, 35.48; H, 5.19.  $^1H$  NMR, ( $CD_2Cl_2$ ):  $\delta$  4.21 [m, 1H,  $C^2H$  of allyl], 3.57 [d (7), 2H,  $H$  syn of allyl], 3.04 [m, 3H,  $PC^1H$ ], 1.47 [m, 18H,  $CH_3$  of  $PPr_3$ ], 1.37 [d (10), 2H,  $H$  anti of allyl].

**[W( $\eta^3-C_3H_5$ )(CO) $_2$ ( $S_2CPCy_3$ )Br] (3a).** A mixture of [W(CO) $_5$ (NCEt) $_3$ ] $^{13}$  (0.11 g, 0.25 mmol) and allyl bromide (30  $\mu$ L, 0.35 mmol) in THF (20 mL) was heated at 60  $^\circ$ C for 1 h. After cooling to room temperature, the solvent was evaporated to afford [W( $\eta^3-C_3H_5$ )(CO) $_2$ (NCEt) $_2$ Br] (ca. 0.25 mmol) as a yellow oil. $^{14}$  This was dissolved in  $CH_2Cl_2$  (20 mL),  $S_2CPCy_3$  (0.357 g, 1 mmol) and  $CS_2$  (1 mL) were added, and the mixture was stirred for 1 h at room temperature. After evaporation of the solvents in vacuo, the greenish-blue residue was extracted with a mixture of  $CH_2Cl_2$ /hexane (1:1, 3  $\times$  20 mL). The combined extracts were filtered, and the filtrate was evaporated in vacuo. The resulting oil was stirred with hexane to afford 3a as a blue-green solid, which was washed with hexane (3  $\times$  10 mL) and  $Et_2O$  (3  $\times$  10 mL). Yield: 0.11 g, 63%. Anal. Calcd for  $C_{24}H_{38}BrO_2PS_2W$ : C, 40.18; H, 5.33. Found: C, 40.40; H, 5.42.  $^1H$  NMR, ( $CD_2Cl_2$ ):  $\delta$  3.45 [m (broad), 3H,  $C^2H$  and  $H$  syn of allyl], 2.69 [m, 3H,  $PC^1H$ ], 1.87–1.26 [m, 32H,  $CH_2$  of  $PCy_3$  and  $H$  anti of allyl].

**[W( $\eta^3-C_3H_5$ )(CO) $_2$ ( $S_2CPPr_3$ )Br] (3b).** To a solution of [W( $\eta^3-C_3H_5$ )(CO) $_2$ (NCEt) $_2$ Br] (ca. 0.25 mmol) in  $CH_2Cl_2$  (20 mL), prepared as described above, was added  $CS_2$  (2 mL, excess), and then  $PPr_3$  (30  $\mu$ L, 0.25 mmol). The stirring time and workup were as described for compound 3a. Yield: 0.08 g, 56%. Anal. Calcd for  $C_{15}H_{26}BrO_2PS_2W$ : C, 30.17; H, 4.39. Found: C, 30.24; H, 4.45.  $^1H$  NMR, ( $CD_2Cl_2$ ):  $\delta$  3.46 [m (broad), 3H,  $C^2H$  and  $H$  syn of allyl], 3.02 [m, 3H,  $PC^1H$ ], 1.47 [m, 18H,  $CH_3$  of  $PPr_3$ ], 1.37 [d (10), 2H,  $H$  anti of allyl].

**[( $\eta^3-C_3H_5$ )(CO) $_2$ Mo( $\mu$ -Br)( $\mu$ - $S_2CPCy_3$ )Mo(CO) $_3$ ] (4a).** [Mo(CO) $_6$ ] (0.106 g, 0.4 mmol) was heated in acetonitrile (20 mL) for 3 h. After cooling the solution, the solvent was evaporated in vacuo to yield solid [Mo(CO) $_3$ (NCMe) $_3$ ] in virtually qualitative yield. To this was added 2a (0.25 g, 0.4 mmol), and the mixture was dissolved in  $CH_2Cl_2$  and stirred for 10 min. The solvent was

evaporated to dryness, and the residue was extracted with the minimum amount of  $CH_2Cl_2$  and filtered. The filtrate was concentrated to ca. 7 mL. Addition of hexane and slow evaporation gave 4a as a red microcrystalline solid. Yield: 0.29 g, 91%. Anal. Calcd for  $C_{27}H_{38}BrMo_2O_5PS_2$ : C, 40.06; H, 4.73. Found: C, 40.21; H, 4.74.  $^1H$  NMR, ( $CD_2Cl_2$ ):  $\delta$  4.13 [tt (10 and 7), 1H,  $C^2H$  of allyl], 3.50 [d (7), 2H,  $H$  syn of allyl], 2.58 [m, 3H,  $PC^1H$ ], 1.95–1.34 [m, 30H,  $CH_2$  of  $PCy_3$ ], 1.13 [d (10), 2H,  $H$  anti of allyl].

**[( $\eta^3-C_3H_5$ )(CO) $_2$ Mo( $\mu$ -Br)( $\mu$ - $S_2CPPr_3$ )Mo(CO) $_3$ ] (4b).** Compound 4b was prepared as described for 4a, by using [Mo(CO) $_6$ ] (0.106 g, 0.4 mmol) and 2b (0.21 g, 0.4 mmol). Yield: 0.23 g, 85%. Anal. Calcd for  $C_{18}H_{26}BrMo_2O_5PS_2$ : C, 31.37; H, 3.80. Found: C, 31.50; H, 3.69.  $^1H$  NMR, ( $CD_2Cl_2$ ):  $\delta$  4.15 [m, 1H,  $C^2H$  of allyl], 3.48 [d (7), 2H,  $H$  syn of allyl], 2.89 [m, 3H,  $PC^1H$ ], 1.51 [dd, (16 and 7), 18H,  $CH_3$  of  $PPr_3$ ], 1.15 [d (10), 2H,  $H$  anti of allyl].

**[( $\eta^3-C_3H_5$ )(CO) $_2$ Mo( $\mu$ -Br)( $\mu$ - $S_2CPCy_3$ )W(CO) $_3$ ] (4c).** A mixture of [W(CO) $_5$ (NCEt) $_3$ ] (0.17 g, 0.40 mmol) and 2a (0.25 g, 0.4 mmol) in  $CH_2Cl_2$  (20 mL) was stirred for 1 h. The workup was as described above for compound 4a. Yield: 0.24 g, 68%. Anal. Calcd for  $C_{27}H_{38}BrMoO_5PS_2W$ : C, 36.14; H, 4.27. Found: C, 35.93; H, 4.04.  $^1H$  NMR, ( $CD_2Cl_2$ ):  $\delta$  4.16 [m, 1H,  $C^2H$  of allyl], 3.48 [d (6), 2H,  $H$  syn of allyl], 2.56 [m, 3H,  $PC^1H$ ], 1.94–1.36 [m, 30 H,  $CH_2$  of  $PCy_3$ ], 1.08 [d (10), 2H,  $H$  anti of allyl].

**[( $\eta^3-C_3H_5$ )(CO) $_2$ Mo( $\mu$ -Br)( $\mu$ - $S_2CPPr_3$ )W(CO) $_3$ ] (4d).** Compound 4d was prepared as described for 4c, by using [W(CO) $_5$ (NCEt) $_3$ ] (0.17 g, 0.40 mmol) and 2b (0.21 g, 0.4 mmol). Yield: 0.18 g, 60%. Anal. Calcd for  $C_{18}H_{26}BrMoO_5PS_2W$ : C, 27.82; H, 3.37. Found: C, 28.21; H, 3.53.  $^1H$  NMR, ( $CD_2Cl_2$ ):  $\delta$  4.18 [m, 1H,  $C^2H$  of allyl], 3.46 [d (6), 2H,  $H$  syn of allyl], 2.82 [m, 3H,  $PC^1H$ ], 1.49 [dd (16 and 7), 18 H,  $CH_3$  of  $PPr_3$ ], 1.09 [d (10), 2H,  $H$  anti of allyl].

**[( $\eta^3-C_3H_5$ )(CO) $_2$ W( $\mu$ -Br)( $\mu$ - $S_2CPCy_3$ )Mo(CO) $_3$ ] (5a).** Compound 5a was prepared as described above for 4a, from [Mo(CO) $_6$ ] (0.07 g, 0.25 mmol) and 3a (0.18 g, 0.25 mmol). Yield: 0.19 g, 86%. Anal. Calcd for  $C_{27}H_{38}BrMoO_5PS_2W$ : C, 36.14; H, 4.27. Found: C, 35.82; H, 4.12.  $^1H$  NMR, ( $CD_2Cl_2$ ):  $\delta$  3.33 [m (br), 3H,  $C^2H$  and  $H$  syn of allyl], 2.57 [m, 3H,  $PC^1H$ ], 1.93–1.38 [m, 32 H,  $CH_2$  of  $PCy_3$  and  $H$  anti of allyl].

**[( $\eta^3-C_3H_5$ )(CO) $_2$ W( $\mu$ -Br)( $\mu$ - $S_2CPPr_3$ )Mo(CO) $_3$ ] (5b).** Compound 5b was prepared as described above for 4a, from [Mo(CO) $_6$ ] (0.07 g, 0.25 mmol) and 3b (0.15 g, 0.25 mmol). Yield: 0.16 g, 80%. Anal. Calcd for  $C_{18}H_{26}BrMoO_5PS_2W$ : C, 27.82; H, 3.37. Found: C, 27.55; H, 3.21.  $^1H$  NMR, ( $CD_2Cl_2$ ):  $\delta$  3.33 [m (br), 3H,  $C^2H$  and  $H$  syn of allyl], 2.89 [m, 3H,  $PC^1H$ ], 1.59 [d (7), 2H,  $H$  anti of allyl], 1.49 [dd (16 and 7), 18 H,  $CH_3$  of  $PPr_3$ ].

**[( $\eta^3-C_3H_5$ )(CO) $_2$ W( $\mu$ -Br)( $\mu$ - $S_2CPCy_3$ )W(CO) $_3$ ] (5c).** A mixture of [W(CO) $_5$ (NCEt) $_3$ ] (0.11 g, 0.25 mmol) and 3a (0.18 g, 0.25 mmol) in  $CH_2Cl_2$  (20 mL), was stirred for 1 h at room temperature. The solvent was evaporated to dryness, and the residue was extracted with  $CH_2Cl_2$ /hexane (1:1, 3  $\times$  15 mL), and filtered. Slow evaporation of the filtrate gave 5c as a red microcrystalline solid. Yield: 0.20 g, 82%. Anal. Calcd for  $C_{27}H_{38}BrO_5PS_2W_2$ : C, 32.91; H, 3.89. Found: C, 33.24; H, 4.00.  $^1H$  NMR, ( $CD_2Cl_2$ ):  $\delta$  3.53 [m (br), 3H,  $C^2H$  and  $H$  syn of allyl], 2.65 [m, 3H,  $PC^1H$ ], 1.95–1.27 [m, 32 H,  $CH_2$  of  $PCy_3$  and  $H$  anti of allyl].

**[( $\eta^3-C_3H_5$ )(CO) $_2$ W( $\mu$ -Br)( $\mu$ - $S_2CPPr_3$ )W(CO) $_3$ ] (5d).** Compound 5d was prepared as described above for 5c, from [W(CO) $_5$ (NCEt) $_3$ ] (0.11 g, 0.25 mmol) and 3b (0.15 g, 0.25 mmol). Yield: 0.17 g, 76%. Anal. Calcd for  $C_{18}H_{26}BrO_5PS_2W_2$ : C, 24.99; H, 3.03. Found: C, 25.36; H, 3.12.  $^1H$  NMR, ( $CD_2Cl_2$ ):  $\delta$  3.29 [m, (br), 3H,  $C^2H$  and  $H$  syn of allyl], 2.81 [m, 3H,  $PC^1H$ ], 1.69–1.24 [m, 20 H,  $CH_3$  of  $PPr_3$  and  $H$  anti of allyl].

**X-ray Diffraction Study of 4a.** Crystals suitable for an x-ray determination were grown by slow diffusion of hexane into a concentrated solution of compound 4a in  $CH_2Cl_2$ . Relevant crystallographic details are given in Table 3. Unit cell parameters were determined from the least-squares refinement of a set of 25 centered reflections. Three reflections were measured every 1 h as orientation and intensity control. Significant decay of the intensity was not observed. Heavy atoms were located from a Patterson synthesis, and the remaining non-hydrogen atoms by

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Table 1. IR and  $^{31}\text{P}\{^1\text{H}\}$  NMR Data for the New Complexes

compd	IR ( $\text{CH}_2\text{Cl}_2$ ) $\nu(\text{CO})$ , $\text{cm}^{-1}$	$^{31}\text{P}\{^1\text{H}\}$ NMR <sup>a</sup> ( $\text{S}_2\text{CP}$ )
2a, $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{S}_2\text{CPCy}_3)\text{Br}]$	1941 (vs), 1860 (s)	25.2
2b, $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{S}_2\text{CPr}^i_3)\text{Br}]$	1942 (vs), 1861 (s)	35.6
3a, $[\text{W}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{S}_2\text{CPCy}_3)\text{Br}]$	1932 (vs), 1851 (s)	32.3
3b, $[\text{W}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{S}_2\text{CPr}^i_3)\text{Br}]$	1933 (vs), 1853 (s)	41.9
4a, $[(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2\text{Mo}(\mu\text{-Br})(\mu\text{-S}_2\text{CPCy}_3)\text{Mo}(\text{CO})_3]$	2023 (s), 1946 (vs), 1856 (s)	36.6
4b, $[(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2\text{Mo}(\mu\text{-Br})(\mu\text{-S}_2\text{CPr}^i_3)\text{Mo}(\text{CO})_3]$	2024 (s), 1947 (vs), 1853 (s)	48.3
4c, $[(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2\text{Mo}(\mu\text{-Br})(\mu\text{-S}_2\text{CPCy}_3)\text{W}(\text{CO})_3]$	2016 (s), 1941 (vs), 1852 (s)	35.0
4d, $[(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2\text{Mo}(\mu\text{-Br})(\mu\text{-S}_2\text{CPr}^i_3)\text{W}(\text{CO})_3]$	2017 (s), 1942 (vs), 1853 (s)	46.9
5a, $[(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2\text{W}(\mu\text{-Br})(\mu\text{-S}_2\text{CPCy}_3)\text{Mo}(\text{CO})_3]$	2025 (s), 1949 (vs), 1934 (vs), 1864 (m), 1833 (m)	37.8
5b, $[(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2\text{W}(\mu\text{-Br})(\mu\text{-S}_2\text{CPr}^i_3)\text{Mo}(\text{CO})_3]$	2026 (s), 1947 (sh), 1934 (vs), 1865 (m), 1836 (m)	49.5
5c, $[(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2\text{W}(\mu\text{-Br})(\mu\text{-S}_2\text{CPCy}_3)\text{W}(\text{CO})_3]$	2018 (s), 1935 (vs), 1856 (m), 1839 (m)	36.1
5d, $[(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2\text{W}(\mu\text{-Br})(\mu\text{-S}_2\text{CPr}^i_3)\text{W}(\text{CO})_3]$	2020 (s), 1937 (vs), 1857 (m), 1839 (m)	47.7

<sup>a</sup>  $\text{CDCl}_3$  solutions;  $\delta$  (ppm) from external  $\text{H}_3\text{PO}_4$  (85%, aq).

Table 2.  $^{13}\text{C}\{^1\text{H}\}$  NMR Data for the New Complexes<sup>a</sup>

compd	$\text{M}^0\text{-CO}$	$\text{M}^{\text{II}}\text{-CO}$	$\text{S}_2\text{C-P}$	allyl		$\text{PR}_3$
				CH	$\text{CH}_2$	
4a	241.8 [d (6)], 217.4	226.3	90.5 [d (46)]	76.1	59.4	R = Cy: 33.5 [d (49), $\text{C}^1$ ], 27.4 [ $\text{C}^2$ and $\text{C}^6$ ], 26.8 [d (12), $\text{C}^3$ and $\text{C}^5$ ], 25.2 [ $\text{C}^4$ ]
4b	241.6 [d (6)], 217.2	226.3	90.0 [d (47)]	76.6	59.2	R = Pr <sup>i</sup> : 23.4 [d (41), CH], 17.9 [ $\text{CH}_3$ ]
4c	233.6 [d (5)], 215.4	226.6	80.8 [d (48)]	76.1	59.3	R = Cy: 33.5 [d (40), $\text{C}^1$ ], 27.5 [d (3), $\text{C}^2$ and $\text{C}^6$ ], 26.7 [d (12), $\text{C}^3$ and $\text{C}^5$ ], 25.2 [ $\text{C}^4$ ]
4d	233.6 [d (5)], 215.1 <sup>b</sup>	226.6	80.0 [d (49)]	76.0	59.1	R = Pr <sup>i</sup> : 23.4 [d (42), CH], 18.0 [ $\text{CH}_3$ ]
5a	241.5 [d (5)], 217.7	218.5	91.5 [d (44)]	68.3	52.2	R = Cy: 33.5 [d (39), $\text{C}^1$ ], 27.3 [ $\text{C}^2$ and $\text{C}^6$ ], 26.7 [d (12), $\text{C}^3$ and $\text{C}^5$ ], 25.1 [ $\text{C}^4$ ]
5b	241.5 [d (6)], 217.7	218.2	90.6 [d (40)]	68.3	51.9	R = Pr <sup>i</sup> : 23.4 [d (41), CH], 17.8 [ $\text{CH}_3$ ]
5c	233.3 [d (5)], 216.4	217.9	82.1 [d (46)]	68.2	51.9	R = Cy: 33.6 [d (39), $\text{C}^1$ ], 27.4 [ $\text{C}^2$ and $\text{C}^6$ ], 26.8 [d (12), $\text{C}^3$ and $\text{C}^5$ ], 25.3 [ $\text{C}^4$ ]
5d	232.5 [d (5)], 217.1	218.2	82.4 [d (47)]	68.5	50.0	R = Pr <sup>i</sup> : 23.42 [d (42), CH], 17.96 [ $\text{CH}_3$ ]

<sup>a</sup> Taken from  $\text{CD}_2\text{Cl}_2$  solutions. <sup>b</sup> Singlet with satellites,  $J(^{183}\text{W}\text{-}^{13}\text{C}) = 160$  Hz.

Table 3. Crystallographic Data for  $[(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2\text{Mo}(\mu\text{-Br})(\mu\text{-S}_2\text{CPCy}_3)\text{Mo}(\text{CO})_3]$  (4a)

formula	$\text{C}_{27}\text{H}_{38}\text{BrMo}_2\text{O}_5\text{PS}_2$
fw	808.47
cryst syst, space group	triclinic, $P\bar{1}$
a, Å	10.037(5)
b, Å	10.669(5)
c, Å	15.323(6)
$\alpha$ , deg	84.52(3)
$\beta$ , deg	78.40(3)
$\gamma$ , deg	82.01(4)
$V$ , Å <sup>3</sup>	1588(1)
Z	2
T, K	293
$\rho_{\text{calc}}$ , $\text{g cm}^{-3}$	1.69
$F(000)$	812
$\lambda(\text{Mo K}\alpha)$ , Å	0.710 73
$\mu$ , $\text{cm}^{-1}$	22.27
cryst size, mm; color	$0.3 \times 0.13 \times 0.1$ ; red
method of collcn	$\omega/2\theta$ scan
scan range, deg	$2 \leq \theta \leq 25$
collcn limits	$-11 \leq h \leq 11, -12 \leq k \leq 12, 0 \leq l \leq 18$
no. of reflns collcd	5808
no. of reflns obsd	2874 [ $I \geq 3\sigma(I)$ ]
no. of params	362
data to param ratio	7.93
weighting scheme	$w = [\sigma^2(F) + gF^2]^{-1}$
g	0.0012
residuals R, $R_w$	0.042, 0.043

DIRDIF.<sup>15</sup> Full matrix least-squares refinement was made with SHELX.<sup>16</sup> After isotropic refinement, an absorption correction was applied with DIFABS.<sup>17</sup> All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were geometrically positioned using a riding model, with a common isotropic temperature factor which was refined.

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## Results and Discussion

Complex  $[\text{Mo}(\eta^3\text{-allyl})(\text{CO})_2(\text{NCMe})_2\text{Br}]$  (1a) reacts with  $\text{S}_2\text{CPR}_3$  in dichloromethane to afford solutions from which new compounds of formula  $[\text{Mo}(\eta^3\text{-allyl})(\text{CO})_2(\text{S}_2\text{CPR}_3)\text{Br}]$  (R = Cy, 2a; R = Pr<sup>i</sup>, 2b) can be isolated as blue microcrystalline solids. These complexes have been characterized by analytical and spectroscopic data. Their IR spectra (see Table 1) display two  $\nu(\text{CO})$  bands at frequencies close to those of the starting 1a, while their  $^1\text{H}$  NMR spectra show the signals characteristic of the allyl ligand: one multiplet for the hydrogen bonded to the central carbon, one doublet for the *anti* protons and one doublet for the *syn* protons. The analogous tungsten complexes,  $[\text{W}(\eta^3\text{-allyl})(\text{CO})_2(\text{S}_2\text{CPR}_3)\text{Br}]$  (R = Cy, 3a; R = Pr<sup>i</sup>, 3b) were obtained by a similar procedure, by reacting  $[\text{W}(\eta^3\text{-allyl})(\text{CO})_2(\text{NCMe})_2\text{Br}]$  (1b) with  $\text{S}_2\text{CPR}_3$ . The low solubility of mononuclear complexes 2a,b and 3a,b precluded the acquisition of good  $^{13}\text{C}$  NMR spectra for them.

Complexes  $[\text{M}^{\text{II}}(\eta^3\text{-allyl})(\text{CO})_2(\text{S}_2\text{CPR}_3)\text{Br}]$  (M = Mo, 2a,b; M = W, 3a,b) react with  $[\text{M}^0(\text{CO})_3(\text{nitrile})_3]$  ( $\text{M}^0 = \text{Mo}$ , nitrile = NCMe;  $\text{M}^0 = \text{W}$ , nitrile = NCEt) to afford dinuclear complexes  $[(\text{CO})_2(\eta^3\text{-allyl})\text{M}^{\text{II}}(\mu\text{-Br})(\mu\text{-S}_2\text{CPR}_3)\text{M}^0(\text{CO})_3]$  (4a-d and 5a-d; see Scheme 1), which can be isolated as red crystalline solids. All of them have been characterized by analytical and spectroscopic data (see Experimental Section, Tables 1 and 2). While the  $^{31}\text{P}$  and  $^{13}\text{C}$  NMR spectra of complexes 4a-d and 5a-d show similar features, thus indicating that all of them are isostructural, it is noticeable that their IR spectra display different numbers of  $\nu(\text{CO})$  bands, depending on the fragments included in the molecule. Thus, five bands are observed for complexes 5a,b, containing the  $(\eta^3\text{-allyl})\text{W}^{\text{II}}(\text{CO})_2$  and  $\text{Mo}^0(\text{CO})_3$  fragments, as expected for dinuclear pentacarbonyls of symmetry  $\text{C}_1$  (see below for the structure determination of one of the derivatives). The coincidence of two  $\nu(\text{CO})$  frequencies in the region of 1935–1937  $\text{cm}^{-1}$  produces a pattern of four bands for complexes 5c-d, which contain  $(\eta^3\text{-allyl})\text{W}^{\text{II}}(\text{CO})_2$  and  $\text{W}^0(\text{CO})_3$ . Finally, another coincidence of two vibrations in the 1852–1856  $\text{cm}^{-1}$  region

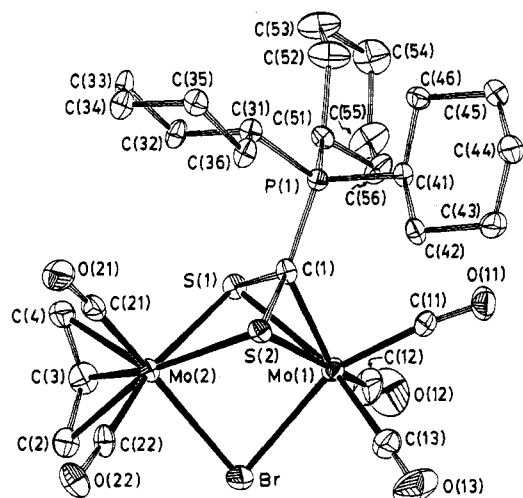
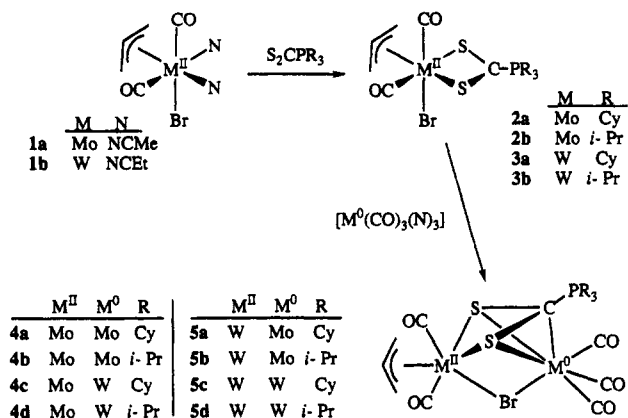


Figure 1. Perspective view (EUCLID Package)<sup>21</sup> of the structure of  $[(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2\text{Mo}(\mu\text{-Br})(\mu\text{-S}_2\text{CPCy}_3)\text{Mo}(\text{CO})_3]$  (**4a**), showing the atom numbering.

Scheme 1



accounts for the pattern of three bands observed for complexes **4a–d** containing  $(\eta^3\text{-allyl})\text{Mo}^{\text{II}}(\text{CO})_2$  and  $\text{M}^0(\text{CO})_3$  ( $\text{M} = \text{Mo}$  or  $\text{W}$ ). The intensity and width of the bands are consistent with this analysis.

A crystal of  $[(\text{CO})_2(\eta^3\text{-allyl})\text{Mo}(\mu\text{-Br})(\mu\text{-S}_2\text{CPCy}_3)\text{Mo}(\text{CO})_3]$  (**4a**), was subjected to an X-ray determination, and the results are presented in Figure 1 and in Tables 3 (crystal data), 4 (atomic coordinates), and 5 (selected bond lengths and angles). It can be seen in Figure 1 that the molecule of **4a** consists of the fragments  $\{\text{Mo}(\eta^3\text{-allyl})(\text{CO})_2\}$  and  $\{\text{Mo}(\text{CO})_3\}$  held together by one bromine bridge and one  $\text{S}_2\text{CPCy}_3$  ligand which acts as a  $\eta^2\text{-S,S'}$  chelate toward the molybdenum atom of the allyldicarbonyl fragment and as a  $\eta^3\text{-S,C,S'}$  pseudoallyl to the molybdenum atom of the tricarbonyl fragment.

The geometry of the core  $\text{Mo}(\mu\text{-Br})(\mu\text{-S}_2\text{CPCy}_3)\text{Mo}$  is close to that observed in  $[(\text{CO})_3\text{Mn}(\mu\text{-Br})(\mu\text{-S}_2\text{CPCy}_3)\text{Mo}(\text{CO})_3]$ ,<sup>4</sup> allowing for the different covalent radii of Mn and Mo. As it was found in the Mn–Mo complex, the intermetallic distance of 3.491(2) Å in **4a** is slightly longer than that expected for a molybdenum–molybdenum bond. Thus, distances as long as 3.274(1) Å have been found in dimolybdenum compounds such as  $[\text{Mo}_2(\text{CO})_5(\text{PEt}_3)(\mu\text{-guaiazulene})]$ ,<sup>18</sup> in which the existence of a metal–metal bond is well established.

In the structure found for **4a** in the solid state (Figure 1), the two methylene termini of the allyl group are not

Table 4. Atomic Coordinates for Non-Hydrogen Atoms in  $[(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2\text{Mo}(\mu\text{-Br})(\mu\text{-S}_2\text{CPCy}_3)\text{Mo}(\text{CO})_3]$  (**4a**)

atom	x	y	z	$10^2 U_{\text{eq}}, \text{Å}^2$
Mo(1)	0.37060(9)	0.17457(7)	0.30055(6)	3.20(3)
Mo(2)	0.16653(8)	0.21463(7)	0.13798(5)	2.86(3)
Br	0.2391(1)	0.39084(9)	0.23895(8)	5.10(4)
C(1)	0.3366(9)	0.0081(8)	0.2458(5)	2.6(3)
S(1)	0.1662(2)	0.0714(2)	0.2855(2)	3.14(8)
S(2)	0.4064(2)	0.0951(2)	0.1469(1)	2.96(7)
C(11)	0.495(1)	0.0702(9)	0.3681(7)	4.0(4)
O(11)	0.5752(8)	0.0192(7)	0.4083(5)	5.9(3)
C(12)	0.290(1)	0.225(1)	0.4230(8)	6.4(5)
O(12)	0.241(1)	0.248(1)	0.4950(6)	10.3(5)
C(13)	0.535(1)	0.270(1)	0.2703(8)	5.9(5)
O(13)	0.6272(9)	0.3253(9)	0.2504(8)	10.4(5)
C(2)	-0.015(1)	0.380(1)	0.1316(8)	4.5(4)
C(3)	-0.053(1)	0.276(1)	0.1904(8)	5.3(4)
C(4)	-0.054(1)	0.163(1)	0.1542(9)	5.3(5)
C(21)	0.160(1)	0.1032(9)	0.0465(7)	4.3(4)
O(21)	0.1579(9)	0.0445(7)	-0.0128(5)	6.7(3)
C(22)	0.207(1)	0.327(1)	0.0302(7)	4.0(4)
O(22)	0.2260(8)	0.3908(7)	-0.0358(5)	5.7(3)
P(1)	0.3816(2)	-0.1633(2)	0.2656(1)	2.48(7)
C(31)	0.3495(9)	-0.2453(8)	0.1746(5)	2.9(3)
C(32)	0.2036(9)	-0.2100(9)	0.1568(6)	3.6(3)
C(33)	0.177(1)	-0.290(1)	0.0860(6)	4.2(4)
C(34)	0.286(1)	-0.2829(9)	0.0000(6)	4.0(4)
C(35)	0.429(1)	-0.3166(9)	0.0198(6)	3.5(3)
C(36)	0.4530(9)	-0.2312(9)	0.0867(5)	3.4(3)
C(41)	0.5587(8)	-0.2087(8)	0.2819(6)	2.6(3)
C(42)	0.6673(9)	-0.1334(8)	0.2212(6)	3.4(3)
C(43)	0.804(1)	-0.1716(9)	0.2520(7)	4.3(4)
C(44)	0.848(1)	-0.3141(9)	0.2494(8)	5.1(4)
C(45)	0.741(1)	-0.3881(9)	0.3048(7)	4.4(4)
C(46)	0.602(1)	-0.3526(8)	0.2751(7)	3.6(3)
C(51)	0.2603(9)	-0.2100(8)	0.3665(5)	3.0(3)
C(52)	0.252(1)	-0.350(1)	0.3841(7)	6.2(5)
C(53)	0.130(1)	-0.375(1)	0.4573(8)	6.8(5)
C(54)	0.140(1)	-0.319(1)	0.5431(8)	7.0(5)
C(55)	0.155(1)	-0.177(1)	0.5271(7)	7.1(5)
C(56)	0.277(1)	-0.155(1)	0.4511(6)	4.8(4)

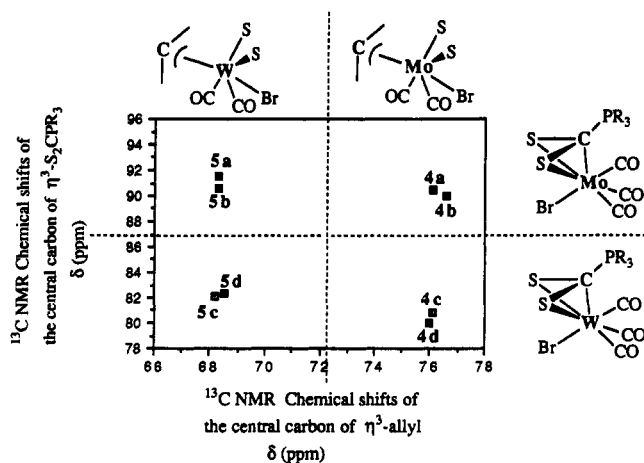
$$^a U_{\text{eq}} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_{ij}$$

equivalent. However, only one signal is observed for the two *anti* hydrogen atoms, as well as for the two *syn*, in the  $^1\text{H}$  NMR spectra in solution. On the other hand, the two carbonyl ligands of the  $\{\text{Mo}(\eta^3\text{-allyl})(\text{CO})_2\}$  moiety produce only one signal in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra, in spite of being nonequivalent in the solid state structure. These facts can be rationalized by assuming the existence of a dynamic process in solution at room temperature, involving the twist of the triangular face formed by the two carbonyls and the allyl group. Such trigonal-twist processes have been proposed in several mononuclear allyl dicarbonyl complexes.<sup>19</sup>

The spectroscopic data available fully support the structures depicted for the complexes in Scheme 1. In the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra there is a fairly good correlation between the position of the signals of the central carbon of the  $\text{S}_2\text{CPR}_3$  ligand and the metal to which it is bonded, and the same occurs with the signal of the central carbon of the  $\eta^3\text{-allyl}$  ligand. In Figure 2, the values of the chemical shifts observed for the central carbon of  $\text{S}_2\text{CPR}_3$  ( $y$ -axis) are plotted against the values of the chemical shifts of the central carbon of the  $\eta^3\text{-allyl}$  ligand ( $x$ -axis). It can be seen that the signal of the allyl carbon appears in the range  $\delta$  68.3–68.5 ppm when bonded to tungsten and  $\delta$  76.0–76.6

(19) One reviewer points out that this explanation is probably correct and asks if it is not possible to exclude reversible bridge breaking. We propose here the trigonal twist process as the most sensible explanation in terms of energy cost. Thus, in related mononuclear complexes, the trigonal twist has a low energy barrier (about 11 kcal mol<sup>-1</sup>).<sup>14</sup> Any process involving the breaking of one or more metal–ligand bonds would have a much higher barrier.

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**Figure 2.** Plot of the chemical shift of the central carbon of  $S_2CPR_3$  against the chemical shift of the central carbon of the  $\eta^3$ -allyl ligand in complexes **4a-d** and **5a-d**.

**Table 5.** Selected Distances (Å) and Angles (deg) for  $[(\eta^3-C_3H_5)(CO)_2Mo(\mu-Br)(\mu-S_2CPCy_3)Mo(CO)_3]$  (**4a**)

Mo(1)-S(1)	2.518(2)	Mo(1)-S(2)	2.519(2)
Mo(2)-S(1)	2.604(2)	Mo(2)-S(2)	2.586(2)
Mo(1)-Br	2.682(1)	Mo(2)-Br	2.801(1)
Mo(1)-C(1)	2.132(8)	Mo(1)-C(11)	1.95(1)
Mo(1)-C(12)	1.98(1)	Mo(1)-C(13)	2.01(1)
Mo(2)-C(21)	1.94(1)	Mo(2)-C(22)	1.95(1)
Mo(2)-C(2)	2.365(9)	Mo(2)-C(3)	2.22(1)
Mo(2)-C(4)	2.32(1)	C(1)-S(1)	1.758(8)
C(1)-S(2)	1.770(8)	C(1)-P(1)	1.832(8)
C(2)-C(3)	1.41(2)	C(3)-C(4)	1.38(2)
C(11)-O(11)	1.16(1)	C(12)-O(12)	1.15(1)
C(13)-O(13)	1.14(1)	C(21)-O(21)	1.16(1)
C(22)-O(22)	1.16(1)		
Mo(2)-Br-Mo(1)	79.05(7)	S(1)-Mo(1)-Br	86.4(1)
S(1)-Mo(1)-S(2)	70.2(1)	S(1)-Mo(1)-C(1)	43.5(2)
S(2)-Mo(1)-Br	88.5(1)	S(2)-Mo(1)-C(1)	43.8(2)
C(1)-Mo(1)-Br	114.6(2)	C(11)-Mo(1)-Br	156.2(3)
C(11)-Mo(1)-C(1)	89.2(3)	C(11)-Mo(1)-S(1)	114.3(3)
C(11)-Mo(1)-S(2)	109.0(3)	C(12)-Mo(1)-Br	87.7(4)
C(12)-Mo(1)-C(1)	125.3(4)	C(12)-Mo(1)-S(1)	94.0(4)
C(12)-Mo(1)-S(2)	164.0(4)	C(12)-Mo(1)-C(11)	79.5(5)
C(13)-Mo(1)-Br	84.0(3)	C(13)-Mo(1)-C(1)	128.8(4)
C(13)-Mo(1)-S(1)	161.5(4)	C(13)-Mo(1)-S(2)	93.7(4)
C(13)-Mo(1)-C(11)	79.0(4)	C(13)-Mo(1)-C(12)	101.4(5)
S(1)-Mo(2)-Br	82.3(1)	S(2)-Mo(2)-Br	84.7(1)
S(2)-Mo(2)-S(1)	67.9(1)	C(2)-Mo(2)-Br	79.5(3)
C(2)-Mo(2)-S(1)	118.7(3)	C(2)-Mo(2)-S(2)	161.6(3)
C(3)-Mo(2)-Br	89.7(3)	C(3)-Mo(2)-S(1)	86.9(3)
C(3)-Mo(2)-S(2)	154.6(3)	C(3)-Mo(2)-C(2)	35.6(4)
C(4)-Mo(2)-Br	123.6(3)	C(4)-Mo(2)-S(1)	83.1(3)
C(4)-Mo(2)-S(2)	136.7(3)	C(4)-Mo(2)-C(2)	61.3(4)
C(4)-Mo(2)-C(3)	35.3(4)	C(21)-Mo(2)-Br	164.7(3)
C(21)-Mo(2)-S(1)	106.3(3)	C(21)-Mo(2)-S(2)	87.0(3)
C(21)-Mo(2)-C(2)	106.1(4)	C(21)-Mo(2)-C(3)	103.1(4)
C(21)-Mo(2)-C(4)	70.6(4)	C(22)-Mo(2)-Br	90.1(3)
C(22)-Mo(2)-S(1)	167.4(3)	C(22)-Mo(2)-S(2)	101.5(3)
C(22)-Mo(2)-C(2)	69.3(4)	C(22)-Mo(2)-C(3)	103.2(4)
C(22)-Mo(2)-C(4)	109.5(4)	C(22)-Mo(2)-C(21)	79.0(4)
S(1)-C(1)-Mo(1)	80.0(3)	S(2)-C(1)-Mo(1)	79.8(3)
S(2)-C(1)-S(1)	110.4(5)	P(1)-C(1)-Mo(1)	136.1(5)
P(1)-C(1)-S(1)	117.4(5)	P(1)-C(1)-S(2)	123.0(4)

ppm when bonded to molybdenum. Similarly, the signal of the central carbon of  $S_2CPR_3$  occurs at  $\delta$  90.0–91.5 ppm when it is bonded to molybdenum and at  $\delta$  80.0–82.4 ppm when bonded to tungsten. Thus, the compounds appear classified in four well-separated domains in the plot of Figure 2. This supports the consistency of the assignment of the signals and, combined with the results of the X-ray structure determination of **4a**, leads to an unambiguous assignment of the structures of complexes **4a-d** and **5a-d**, as depicted in Scheme 1.

In mononuclear complexes containing bidentate  $S,S'$ - $S_2CPR_3$  groups, these ligands act as four electron donors, and also in mononuclear complexes in which  $S_2CPR_3$  ligands are  $\eta^3$ - $S,C,S'$  coordinated. Therefore, it seems to be a reasonable assumption to consider  $S_2CPR_3$  ligands as four-electron donors to each metal in binuclear complexes having  $S_2CPR_3$  bridges coordinated in the  $\eta^2$ - $S,S'$ : $\eta^3$ - $S,C,S'$  fashion and, as a matter of fact, such an electron counting is unambiguous for complexes  $[Mn_2(CO)_6(\mu-S_2CPR_3)]$ .<sup>1</sup> When applying this counting, the EAN rule leads to oxidation numbers Mo(II) for the atom bearing the allyl ligand (to which Br must donate one electron) and Mo(0) for the atom of the  $\{Mo(CO)_3\}$  fragment (to which Br donates two electrons). Thus, in the structure of **4a**, the central carbon of the  $S_2CPCy_3$  ligand prefers to bind Mo(0) instead of Mo(II). We have found this kind of preference in previous work, and we have offered an explanation based on the oxidation numbers of the metal atoms concerned.<sup>4,20</sup> Regarding this point, the structure of **4a** is in agreement with the trends we had observed for other families of compounds: the central carbon of the  $S_2CPCy_3$  ligand in **4a** prefers to form a bond with the metal in the lower oxidation state. As we have discussed above, this can be generalized to all heterobinuclear derivatives **4** and **5**. It can be seen in Scheme 1 that, in all the cases, the compound obtained is the result of the simple displacement of the three nitrile ligands of  $[M^0(CO)_3(\text{nitrile})_3]$  by the  $S,C,S',Br$  donor set of the starting  $[M^{II}(\eta^3\text{-allyl})(CO)_2(S_2CPR_3)Br]$  with the selective formation of a bond between the central carbon of  $S_2CPR_3$  and the metal atom in oxidation state zero. Since this occurs for every combination of metals ( $Mo^{II}/Mo^0$ ,  $Mo^{II}/W^0$ ,  $W^{II}/Mo^0$ , or  $W^{II}/W^0$ ), it can be concluded that the different natures of the metal atoms are not the most important factor governing the preference of the central carbon for one or another of the metals. On the other hand, it strongly supports our argument based on the oxidation states.

## Conclusion

The simple oxidation number formalism is shown to be a useful guide to rationalize the found preference of the central carbon of  $S_2CPR_3$  ligands in homo- and heterobinuclear complexes. In all the known examples the central carbon atom prefers to bind the metal in the lower oxidation state. The  $^{13}C\{^1H\}$  NMR signal of the central carbon of the  $S_2CPR_3$  ligand is a useful diagnostic tool to distinguish the metal to which that central carbon is bonded.

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**Supplementary Material Available:** Complete tables of atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for the structure of **4a** (5 pages). Ordering information is given on any current masthead page.

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