Reactivity of the labile complex [MoCl(η^3-allyl)(CO)$_2$(NCMe)$_2$] with diphosphanes

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The reactions of [MoCl(η^3-allyl)(CO)$_2$(NCMe)$_2$] (**1**) with variable ratios of bis(dimethylphosphanyl)methane (dmpm) or bis(diphenylphosphanyl)methane (dppm) afford different products, in which the diphosphanes are acting either as a chelate, as in [MoCl(η^3-allyl)(CO)$_2$(P–P)] (P–P = dmpm **2**, dppm **6**) and [Mo(NCMe)(η^3-allyl)(CO)$_2$(P–P)]-[{Mo(η^3-allyl)(CO)$_2$}$_2$(μ-Cl)$_3$] (P–P = dmpm **4**, dppm **8**) or as a bridge as in [{Mo(η^3-allyl)(CO)$_2$}$_2$(μ-Cl)$_2$(μ-P–P)] (P–P = dmpm **3**, dppm **7**). The analogous reaction with tetraethyldiphosphite (tedip) affords [{Mo(η^3-allyl)(CO)$_2$}$_2$-(μ-Cl)$_2$(μ-tedip)] (**5**) as a single product.

Introduction

We recently reported that the complex [MoCl(η^3-allyl)(CO)$_2$-(dmpm)] (**2**) (dmpm = bis(dimethylphosphanyl)methane) reacts with carbanionic reagents to afford the corresponding *cis*-dicarbonyl [MoR(η^3-allyl)(CO)$_2$(dmpm)] complexes. These species subsequently rearranged to the isomeric *trans*-dicarbonyl compounds, which then undergo the reductive elimination of the R–allyl coupling products.[1] We have prepared complex **2** by reaction of the known precursor [MoCl(η^3-allyl)(CO)$_2$-(NCMe)$_2$] (**1**)[2] with dmpm, a method that has become conventional for the preparation of [MoCl(η^3-allyl)(CO)$_2$(L–L)] (L–L = bidentate ligand) compounds.[3] However, we observed that traces of other species were formed in addition to complex **2** in some of the preparations. Having ruled out the presence of an impurity in the reagents, we hypothesized that compounds with a molybdenum : dmpm ratio different from 1 : 1 were formed along with complex **2**. Thus, we initiated a careful study of the reaction of the bis(nitrile) complex **1** with dmpm. Our findings are the subject of this paper.

Results and discussion

The reaction of [MoCl(η^3-allyl)(CO)$_2$(NCMe)$_2$] (**1**)[2] with an equimolar amount of dmpm afforded [MoCl(η^3-allyl)-(CO)$_2$(dmpm)] (**2**),[1] which could be isolated in high yield by crystallization. However, the reactions of **1** with substoichiometric amounts of dmpm yielded solutions containing two new compounds in ratios dependent of the amount of dmpm used (Scheme 1). Working with a Mo : dmpm ratio of 2 : 1, complex [{Mo(η^3-allyl)(CO)$_2$}$_2$(μ-Cl)$_2$(μ-dmpm)] (**3**) was obtained as the major product and could be isolated by fractional crystallization. A yellow single crystal of **3** was used for a structural determination by X-ray diffraction. The results are displayed in Fig. 1.

The molecule of **3** consists of two identical *cis*-{Mo-(η^3-allyl)(CO)$_2$} moieties linked by two chloro bridges and a dmpm bridge. Each metal center is electron precise without considering an intermetallic bond; consistently, the Mo–Mo distance (4.027(4) Å) is outside the range of direct Mo–Mo bonds.[4]

The open face of the allyl group on each metal fragment is oriented pointing toward the carbonyls, as found for most mononuclear [MoCl(η^3-allyl)(CO)$_2$(L–L)] derivatives.[5]
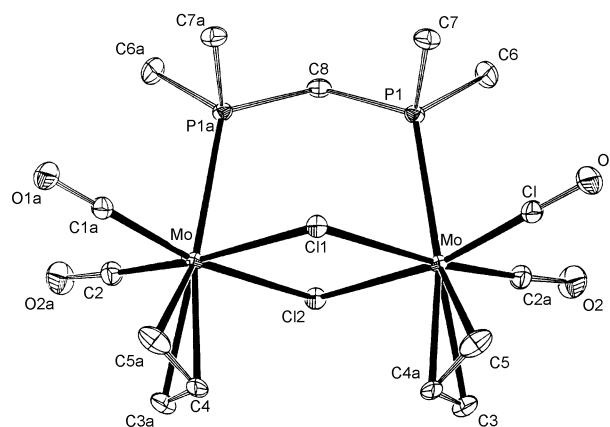

Fig. 1 Thermal ellipsoid plot (30% probability) and numbering scheme of **3**. Selected lengths (Å) and angles (°): Mo–Mo 4.027(4), Mo–Cl(1) 2.627(1), Mo–Cl(2) 2.627(1); Cl(2)–Mo–Cl(1) 79.10(4).

The molecule of **3** possesses a mirror plane orthogonal to the intermetallic vector. The ^{1}H and ^{31}P NMR data (see Experimental section) are consistent with this structure being maintained in solution.

When the reaction of **1** and dmpm was carried out using an Mo : dmpm ratio of 3 : 1, the compound [Mo(NCMe)-(η^3-allyl)(CO)$_2$(dmpm)][{Mo(η^3-allyl)(CO)$_2$}$_2$(μ-Cl)$_3$] (**4**) was the major product. Selective crystallization allowed its isolation, and a structural determination was carried out using single-crystal X-ray diffraction. The results are displayed in Fig. 2.

Compound **4** is a salt whose anion, consisting of two *cis*-{Mo(η^3-allyl)(CO)$_2$} fragments linked by three chloro bridges, was previously found in the compound [Mo(η^3-allyl)(CO)$_2$-(NCMe)$_3$][{Mo(η^3-allyl)(CO)$_2$}$_2$(μ-Cl)$_3$].[6] The cation of **4** is a monometallic complex with an acetonitrile and a chelating dmpm ligand bonded to a {Mo(η^3-allyl)(CO)$_2$} fragment.[7] Obviously, the formation of **4** is the result of ionization and intermolecular chloride transfer. This has also been found to be the case in the generation of the mentioned salt [Mo(η^3-allyl)-(CO)$_2$(NCMe)$_3$][{Mo(η^3-allyl)(CO)$_2$}$_2$(μ-Cl)$_3$] when the labile precursor **1** stands in solution of non-coordinating solvents prolonged times.[6] However, there should be noted that the formation of the salt **4** upon reaction of **1** with dmpm is
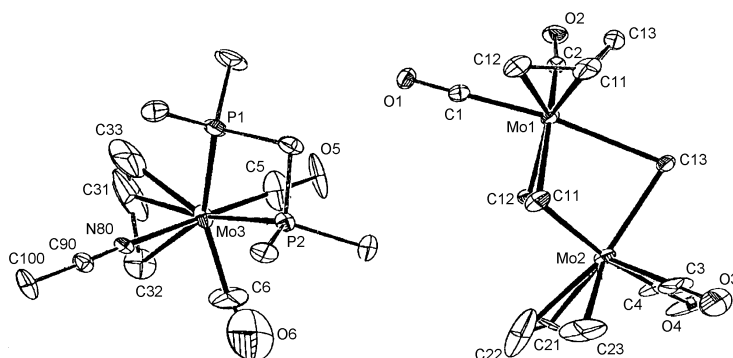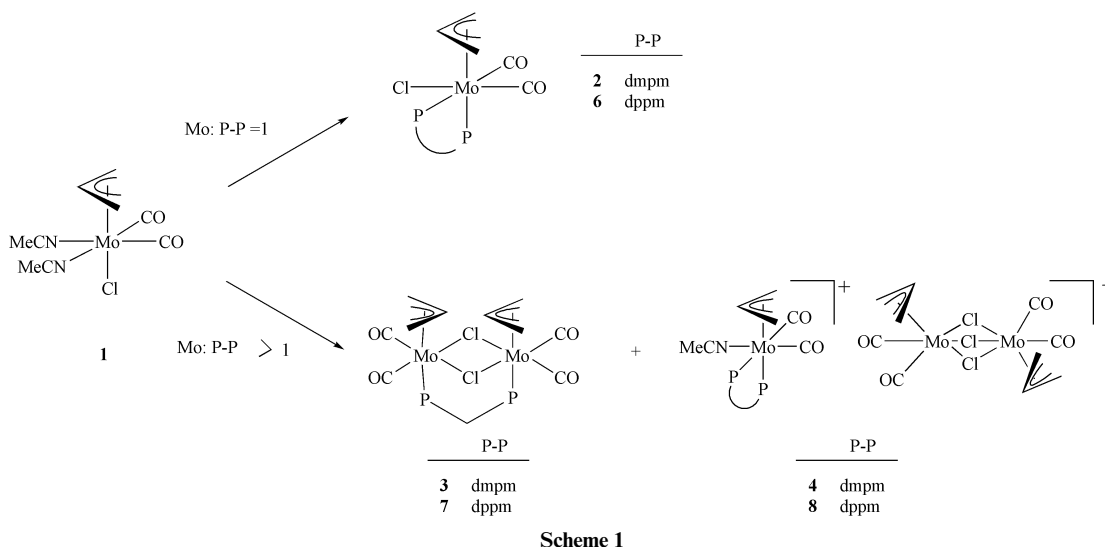
Scheme 1

Fig. 2 Thermal ellipsoid plot (30% probability) and numbering scheme of **4**. Selected bond lengths (Å) and angles (°): Mo(1)–Cl(1) 2.519(2), Mo(1)–Cl(2) 2.596(2), Mo(1)–Cl(3) 2.580(3), Mo(2)–Cl(1) 2.566(2), Mo(2)–Cl(2) 2.538(2), Mo(2)–Cl(3) 2.580(2), Mo(1)–C(1) 1.931(10), Mo(3)–N(80) 2.220(8); Mo(3)–N(1) 2.212(8), Mo(3)–P(1) 2.458(3), Mo(3)–P(2) 2.463(3), Cl(3)–Mo(2)–Cl(2) 78.20(7), Cl(1)–Mo(2)–Cl(2) 78.03(7), Cl(2)–Mo(1)–Cl(3) 79.39(8), Cl(1)–Mo(1)–Cl(3) 77.64(8), N(1)–Mo(3)–P(1) 91.8(2), N(1)–Mo(3)–P(2) 91.5(2), P(1)–Mo(3)–P(2) 66.59(9).

instantaneous. This suggests that the presence of the strongly donating dmpm ligand promotes the ionization.

Using ^{31}P NMR, we have examined how the composition of the mixtures obtained by reaction of **1** and dmpm changes with time. We found that the final formation of the dmpm-bridged bimetallic complex **3** takes place, at least in part, at the expense of the salt **4**, which, even using a Mo : dmpm ratio of 2 : 1, is initially formed as the major product. The formation of **3** from **4** implies, besides chloride transfer between molybdenum centers, a change in the coordination mode of dmpm, a process that is known to be facile for this diphosphane.[8] Although slower than the formation of **3** from **4**, ^{31}P NMR monitoring indicated that, in the presence of excess of dmpm, the binuclear complex **3** transforms into **2**.

We reasoned that using a diphosphane which is both a poor donor and a good binucleating ligand would favor the formation of a bridged bimetallic complex like **3**. To test this idea, we have chosen tetraethyldiphosphite (tedip), which is a weaker donor than bis(dialkylphosphanyl)alkanes and shows a high preference for the bridging over the chelate coordination mode. Indeed, the reaction of **1** with tedip yielded, regardless of the Mo : tedip ratio, complex $[\{Mo(\eta^3\text{-allyl})(CO)_2\}_2(\mu\text{-Cl})_2\text{-}(\mu\text{-tedip})]$ (**5**) (Scheme 2), which was found to be isostructural with **3** by the results of a single crystal X-ray determination, shown in Fig. 3.

Compounds **3** and **5** are the first examples of diphosphane-bridged complexes with pseudo-octahedral $\{Mo(\eta^3\text{-allyl})\text{-}(CO)_2\}$ moieties.

The formation of similar species in the reactions of **1** with bis(diphenylphosphanyl)methane (dppm), which have been previously used to prepare the well known [MoCl(η^3-allyl)-
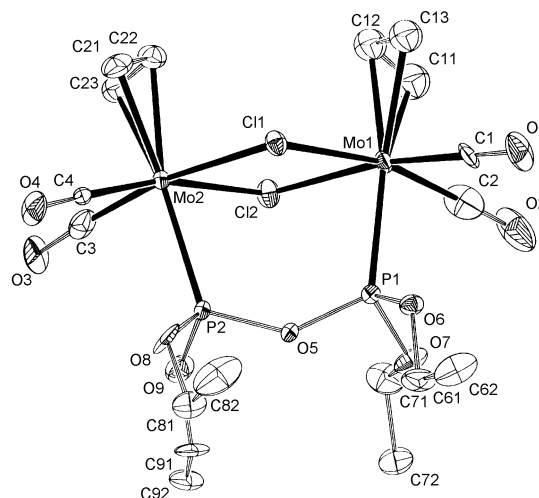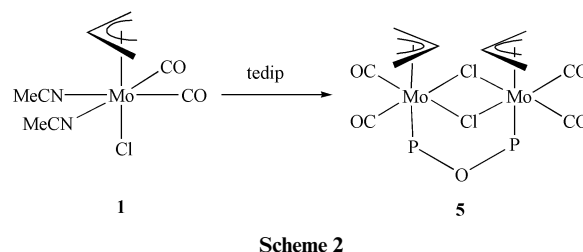

Scheme 2

Fig. 3 Thermal ellipsoid plot (30% probability) and numbering scheme of **5**. Selected lengths (Å) and angles (°): Mo–Mo 3.985(2), Mo–Cl(1) 2.592(2), Mo–Cl(2) 2.588(3); Cl(2)–Mo–Cl(1) 79.45(6).

(CO)$_2$(dppm)]^{3c} complex, was not investigated previously. We set out to explore the possible presence of these species in the crude reaction mixtures obtained from **1** and dppm. Faller *et al.* reported the preparation of [MoCl(η^3-allyl)(CO)$_2$(dppm)] by reaction of **1** with dppm followed by chromatographic purification.^{3c} Accordingly, we found that using a Mo : dppm ratio of 1 : 1, the main product (as shown by the ^{31}P NMR spectrum) was [MoCl(η^3-allyl)(CO)$_2$(dppm)] (**6**), characterized by X-ray diffraction (Fig. 4) (Scheme 1). The structure of **6** is, in the main, similar to that of the previously characterized 1,2-diphenylphosphanylethane (dppe) derivative [MoCl(η^3-allyl)-(CO)$_2$(dppe)].^{3c} In addition, we have observed signals due to two minor products in the ^{31}P NMR spectra of the crude mixtures present before chromatography. The relative amount of these byproducts increased when Mo : dppm ratios of 2 : 1 or 3 : 1 were employed. One of these species, featuring a singlet at −2.33 ppm, was found to be the kinetic product and, by analogy with the results obtained with dmpm (*vide supra*), was believed to be the salt [Mo(NCMe)(η^3-allyl)(CO)$_2$(dppm)]-[{Mo(η^3-allyl)(CO)$_2$}$_2$(μ-Cl)$_3$] (**8**). ^{31}P NMR monitoring of the reaction mixtures showed an increase of two additional compounds featuring singlets at 13.02 and −2.03 ppm. The latter corresponds to the mononuclear complex **6** (*vide supra*). The former could be obtained as the main product using a Mo : dppm ratio of 2 : 1. This product was found to be [{Mo(η^3-allyl)(CO)$_2$}$_2$(μ-Cl)$_2$(μ-dppm)] (**7**) by X-ray diffraction (see Fig. 5). The main features of the structure of **7** are similar to those of **3** (*vide supra*). The interconversions of **6**, **7** and **8** parallel those found for the dmpm analogs (see above).
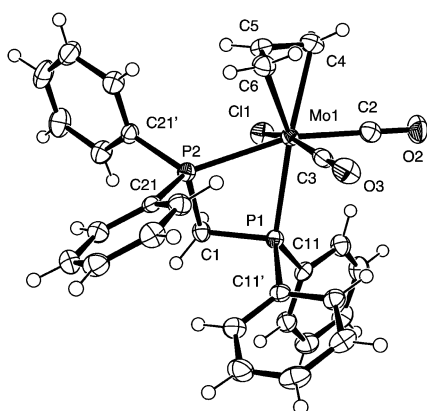

Fig. 4 Thermal ellipsoid plot (30% probability) and numbering scheme of **6**. Selected bond lengths (Å) and angles (°): Mo–Cl 2.5232(9), Mo–P(1) 2.5474(10), Mo–P(2) 2.6015(9), Mo–C(2) 1.973(3), Mo–C(3) 1.941(3); P(1)–Mo–P(2) 64.47(3).
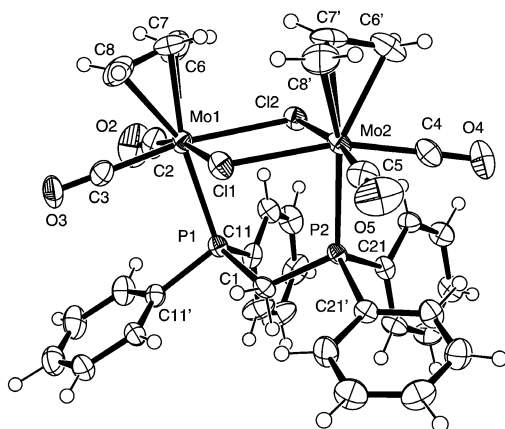

Fig. 5 Thermal ellipsoid plot (30% probability) and numbering scheme of **7**. Selected bond lengths (Å) and angles (°): Mo(1)–Cl(1) 2.5793(11), Mo(1)–Cl(2) 2.6266(14), Mo(2)–Cl(1) 2.5789(13), Mo(2)–Cl(2) 2.6177(11); Cl(2)–Mo–Cl(1) 78.85(5).

In conclusion, the present work indicates that widely used diphosphanes act both as chelates and as bridges toward {Mo(η^3-allyl)(CO)$_2$} fragments, and that chloride transfer, ionization and binucleation can occur readily in solution. The existence of these processes can be of relevance when studying the solution behavior of [MoX(η^3-allyl)(CO)$_2$(P–P)] complexes, which have been used as allylic alkylation precatalysts.[9]

Experimental

All operations were carried out under an atmosphere of dry dinitrogen using Schlenk techniques. Solvents were dried over Na (hexane), CaH$_2$ (CH$_2$Cl$_2$ and MeOH) and distilled immediately before being used. IR spectra were registered in THF solutions. NMR chemical shifts (δ) are given in ppm, and coupling constants (J) in Hz. Apparent triplet is abbreviated "at" in the ^{1}H NMR spectra. All spectra were recorded at room temperature.

Preparation of [MoCl(η^3-C$_3$H$_5$)(CO)$_2$(dmpm)] (2)

The addition of dmpm (50 μL, 0.32 mmol) to [MoCl-(η^3-C$_3$H$_5$)(CO)$_2$(NCMe)$_2$] (**1**)^2 (0.10 g, 0.32 mmol) in CH$_2$Cl$_2$ (10 mL) gave a red solution which was stirred for 5 min. The volume was reduced *in vacuo* to one third and hexane was added to precipitate **2** as an orange crystalline solid. Yield: 0.11 g, 94%; Anal. Calc. for C$_{10}$H$_{19}$ClMoO$_2$P$_2$: C, 32.94; H, 5.25. Found C, 32.61; H, 5.62%. IR (ν_{CO}) (CH$_2$Cl$_2$): 1944s, 1845s cm^{-1}; ^{1}H NMR (CD$_2$Cl$_2$): δ 1.65 [at, $^2J_{P-H}$ = 5, 6H, CH$_3$ dmpm], 1.73 [at, $^2J_{P-H}$ = 5, 6H, CH$_3$ dmpm], 2.31 [d, $^3J_{H-H}$ = 12, 2H, H$_{anti}$], 3.24 [m, 2H, CH$_2$ dmpm], 3.69 [m, 2H, H$_{syn}$], 4.75 [m, 1H, C^{2}H]. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 13.40 [at, $^1J_{P-C}$ = 13, CH$_3$ dmpm], 17.34 [at, $^1J_{P-C}$ = 14, CH$_3$ dmpm], 40.65 [at, $^1J_{P-C}$ = 23, CH$_2$ dmpm], 62.36 [s, C^{1,3} allyl], 98.68 [s, C^2 allyl], 226.68 [at, $^2J_{P-C}$ = 8, CO]. P{^{1}H} NMR (CD$_2$Cl$_2$): δ −24.38.

Reaction of 1 with substoichiometric amounts of dmpm

(a) dmpm (25 μL, 0.16 mmol) was added to a solution of **1** (0.10 g, 0.32 mmol) in CH$_2$Cl$_2$ (20 mL) and the mixture was stirred for 15 min. The solution was concentrated to 5 mL and hexane was added (20 mL), causing the precipitation of an orange solid which was washed with hexane and dried *in vacuo*. By slow diffusion of hexanes into a concentrated solution of the orange solid in CH$_2$Cl$_2$ (5 mL) at −20 °C red crystals of **3** were obtained. Yield: 0.05 g, 60%. Anal. Calc. for C$_{15}$H$_{24}$Cl$_2$Mo$_2$-O$_4$P$_2$: C, 30.37; H, 4.07. Found: C, 30.14; H, 4.21%. IR (ν_{CO}) (CH$_2$Cl$_2$): 1934s, 1851s cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ 1.82 [d, $^3J_{H-H}$ = 10.0, 4H, H$_{syn}$], 1.88 [d, $^2J_{H-P}$ = 7.0, 12H, CH$_3$ dmpm], 2.15 [t, $^2J_{H-P}$ = 12, 2H, CH$_2$ dmpm], 3.71 [d, $^3J_{H-H}$ = 7.0, 4H, H$_{anti}$], 4.68 [m, 2H, C^{2}H]. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ −2.29.

(b) dmpm (16 μL, 0.10 mmol) was added to a solution of **1** (0.10 g, 0.32 mmol) in CH$_2$Cl$_2$ (20 mL) and the mixture was stirred for 15 min. The solution was concentrated to 5 mL, layered with hexane (20 mL) and placed at −20 °C. After several days, orange crystals of **4** were obtained. Yield: 0.03 g, 41%. Anal. Calc. for C$_{22}$H$_{32}$Cl$_3$Mo$_3$NO$_6$P$_2$: C, 28.33; H, 3.45. Found: C, 28.26; H, 3.65%. IR (ν_{CO}) (CH$_2$Cl$_2$): 1992s, 1935s cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): cation [Mo(η^3-allyl)(CO)$_2$(NCMe)-(dmpm)] δ 1.90 [m, 12H, CH$_3$ dmpm], 2.40 [s, 3H, MeCN], 2.46 [d, $^3J_{H-H}$ = 12.13, 2H, H$_{anti}$], 3.17 [m, 2H, CH$_2$ dmpm], 3.75 [d, $^3J_{H-H}$ = 6, 2H, H$_{syn}$], 5.30 [m, 1H, C^{2}H]. Anion [{Mo-(η^3-allyl)(CO)$_2$}$_2$(μ-Cl)$_3$] δ 0.95 [d, $^3J_{H-H}$ = 9.6, 4H, H$_{anti}$], 3.46 [d, $^3J_{H-H}$ = 6.5, 4H, H$_{syn}$], 3.80 [m, 2H, C^{2}H]. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): Cation [Mo(η^3-allyl)(CO)$_2$(NCMe)(dmpm)] δ 4.52 [s, NC*C*H$_3$], 17.80 [m, CH$_3$ dmpm], 41.71 [t, $^1J_{C-H}$ = 27.5, CH$_2$ dmpm], 63.19 [s, C^{1,3} allyl], 108.55 [s, C^2 allyl], 125.03 [s, N*C*Me], 222.29 [s, CO]. Anion [{Mo(η^3-allyl)(CO)$_2$}$_2$(μ-Cl)$_3$] δ 63.78 [s, C^{1,3} allyl], 83.28 [s, C^2 allyl], 228.86 [s, CO]. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ −24.41.

Preparation of [{Mo(η³-C₃H₅)(CO)₂}₂(μ-Cl)₂(μ-tedip)] (5)

Tedip (0.16 mmol, 40 μL) was added to a solution of [MoCl-(η³-C₃H₅)(CO)₂(NCMe)₂] (0.32 mmol, 0.10 g) in CH₂Cl₂ (20 mL). The color of the solution changed immediately from yellow to red. The solution was concentrated *in vacuo* to 2 mL and hexane was added, causing the precipitation of a red solid which was washed with hexane and dried *in vacuo*. Yield: 0.20 g, 86%. Slow diffusion of hexanes onto a concentrated solution of **5** in THF afforded red crystals, one of which was used for a structural determination by X-ray diffraction. Anal. Calc. for C₁₈H₃₀Cl₂Mo₂O₉P₂: C, 30.23; H, 4.22. Found: C, 30.02; H, 4.53%. IR (ν_{CO}) (CH₂Cl₂): 1948s, 1863s cm⁻¹. ¹H NMR (CD₂Cl₂): δ 1.43 [t, $^2J_{H–P}$ = 7, 12H, CH₃], 1.83 [d, $^3J_{H–H}$ = 10.7, 4H, H$_{anti}$], 3.82 [d, $^3J_{H–H}$ = 6.7, 4H, H$_{syn}$], 3.90 [m, 8H, CH₂], 4.49 [m, 2H, C²H]. ¹³C NMR (CD₂Cl₂): δ 16.46 [s, CH₃], 62.99 [s, CH₂], 64.83 [s, C¹,³ allyl], 74.09 [s, C² allyl], 223.57 [at, $^3J_{C–P}$ = 7.9, CO]. ³¹P{¹H} NMR (CD₂Cl₂): δ 127.29.

Reaction of 1 with dppm

A mixture of dppm (0.24 mmol, 0.09 g) and [MoCl(η³-C₃H₅)-(CO)₂(NCMe)₂] (**1**) (0.48 mmol, 0.15 g) was charged in a Schlenk flask along with a stirbar. After three vacuum–nitrogen cycles, CH₂Cl₂ (30 mL) was added. NMR samples were taken at 1 h intervals by charging 0.5 mL amounts of this reaction mixture into 5 mm NMR tubes containing capillary inserts filled with D₂O as lock signal. ³¹P NMR monitoring indicated initial (1 h) predominance of [MoCl(η³-allyl)(CO)₂(dppm)] (**6**) (singlet at −2.03 ppm) and small amounts of [{Mo(η³-C₃H₅)(CO)₂}₂-(μ-Cl)₂(μ-dppm)] (**7**) and [Mo(NCMe)(η³-C₃H₅)(CO)₂(dppm)]-[{Mo(η³-C₃H₅)(CO)₂}₂(μ-Cl)₃] (**8**) (singlets at 13.02 and −2.33 ppm, respectively). After 1 day, the mixture contains similar amounts of **6** and **7** and a small amount of **8**. After 1 week the major product (approximately 70%) is **7**. At this point the orange solution was filtered through diatomaceous earth, concentrated to a volume of 5 mL and layered with hexane. A mixture of yellow crystals of **6** and orange crystals of **7** was obtained, which were separated by hand under a microscope and characterized by NMR spectroscopy and X-ray diffraction. The spectroscopic data of **6** coincide with those reported by Faller *et al.*[3c]

7: Yield: 0.13 g, 64%. Anal. Calc. for C₃₅H₃₂Cl₂Mo₂O₄P₂: C, 49.96; H, 3.83. Found C, 49.79; H, 3.75%. IR (ν_{CO}) (CH₂Cl₂): 1940vs, 1854s cm⁻¹; ¹H NMR (CD₂Cl₂): δ 1.74 [d, $^3J_{H–H}$ = 10, 4H, H$_{anti}$], 3.52 [t, $^2J_{H–P}$ = 11.5, 2H, CH₂ dppm], 3.85 [d, $^3J_{HH}$ = 7, 4H, H$_{syn}$], 4.66 [m, 2H, C²H], 7.29 [m, 20H, Ph of dppm]. ³¹P{¹H} NMR (CD₂Cl₂): δ 13.20.

X-Ray crystallographic study

Data in common: Bruker AXS SMART 1000 CCD diffractometer, ϕ and ω scans, Mo-Kα radiation (λ = 0.71073 Å), graphite monochromator, T = 295 K. Raw frame data were integrated with the SAINT[10] program. Structures were solved by direct methods with SHELXTL.[11] Semi-empirical absorption correction was done with SADABS.[12] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were set in calculated positions and refined as riding atoms, with a common thermal parameter. All calculations were made with SHELXTL.

Crystal data

3: C₁₅H₂₄Cl₂Mo₂O₄P₂, M = 593.06, orthorhombic, space group *Pnma*, a = 11.8955(11), b = 19.191(6), c = 9.294(2) Å, U = 2121.8(9) Å³, T = 293 K, Z = 4, λ(Mo-Kα) = 0.71073

mm⁻¹, 2142 reflections measured, 2142 unique (R_{int} = 0.0287), $wR2$ = 0.0918.

4: C₂₂H₃₂Cl₃Mo₃NO₆P₂, M = 843.57, monoclinic, space group *P2₁/c*, a = 9.6225(4), b = 16.2346(7), c = 21.4232(7) Å, β = 93.951(2)°, U = 3338.7(2) Å³, T = 293 K, Z = 4, λ(Cu-Kα) = 1.54184 mm⁻¹, 5465 reflections measured, 3526 unique (R_{int} = 0.0675), $wR2$ = 0.1844.

5: C₁₈H₃₀Cl₂Mo₂O₉P₂, M = 715.14, monoclinic, space group *P2₁/c*, a = 10.050(7), b = 11.580(9), c = 23.320(11) Å, β = 97.82(3)°, U = 2689(3) Å³, T = 293 K, Z = 4, λ(Cu-Kα) = 1.54184 mm⁻¹, 3961 reflections measured, 2992 unique (R_{int} = 0.0672), $wR2$ = 0.1726.

6: C₃₄H₃₅ClMoO₃P₂, M = 684.95, monoclinic, space group *P2₁/c*, a = 15.119(5), b = 10.830(5), c = 23.494(5) Å, β = 123.229(5)°, U = 3218(2) Å³, T = 293 K, Z = 4, λ(Cu-Kα) = 1.54084 mm⁻¹, 11578 reflections measured, 6058 unique (R_{int} = 0.0365), $wR2$ = 0.0863.

7: C₃₆H₃₃Cl₂NMo₂O₄P₂, M = 868.35, monoclinic, space group *P2₁/c*, a = 14.763(5), b = 15.343(5), c = 17.538(5) Å, β = 114.96(5)°, U = 3601(2) Å³, T = 293 K, Z = 4, λ(Cu-Kα) = 1.54184 mm⁻¹, 6752 reflections measured, 6752 unique (R_{int} = 0.0375), $wR2$ = 0.0836.

CCDC reference numbers 196132–196136.

See http://www.rsc.org/suppdata/dt/b3/b300350g/ for crystallographic data in CIF or other electronic format.

References

1 J. Pérez, V. Riera, A. Rodríguez and S. García-Granda, *Angew. Chem., Int. Ed.*, 2002, **41**, 1427.
2 H. tom Dieck and H. Friedel, *J. Organomet. Chem.*, 1968, **14**, 375.
3 (*a*) P. K. Baker, *Adv. Organomet. Chem.*, 1996, **40**, 46; (*b*) J. W. Goodyear, C. W. Hemingway, R. W. Harrington, M. R. Wiseman and B. J. Brisdon, *J. Organomet. Chem.*, 2002, **664**, 176; (*c*) of particular relevance to the work reported here is the following paper, which deals with the synthesis and characterization of diphosphane complexes: J. W. Faller, D. A. Haitko, R. D. Adams and D. F. Chodosh, *J. Am. Chem. Soc.*, 1979, **114**, 865; (*d*) for a different way to access Mo–allyl compounds see: A. G. W. Hodson, R. K. Thind and M. McPartlin, *J. Organomet. Chem.*, 2002, **664**, 277.
4 S. W. Kirtley, in *Comprehensive Organometallic Chemistry*, ed. G. Wilkinson, F. G. A. Stone and E. Abel, Pergamon, Oxford, 1982, vol. 3, p. 1091.
5 M. D. Curtis and O. Eisenstein, *Organometallics*, 1984, **3**, 887.
6 (*a*) M. G. Drew, B. J. Brisdon and M. Cartwright, *Inorg. Chim. Acta.*, 1979, **36**, 127; (*b*) for other compounds with this bimetallic anion, see: P. Pinto, E. Barranco, M. J. Calhorda, V. Félix and M. G. B. Drew, *J. Organomet. Chem.*, 2000, **601**, 34.
7 For examples of crystallographically characterized [Mo(η³-allyl)-(NCMe)(CO)₂(P–P)]⁺ compounds, see: (*a*) G.-H. Lee, S.-M. Peng, F.-Ch. Liu, D. Mu and R.-S. Liu, *Organometallics*, 1989, **8**, 402; (*b*) S.-F. Lush, S.-H. Wang, G.-H. Lee, S.-M. Peng, S.-L. Wang and R.-S. Liu, *Organometallics*, 1990, **9**, 1862.
8 F. A. Cotton, E. V. Dikarev and S. Herrero, *Inorg. Chem.*, 1999, **38**, 490.
9 B. M. Trost and M. Lautens, *J. Am. Chem. Soc.*, 1982, **104**, 5543.
10 SAINT+. SAX area detector integration program. Version 6.02. Bruker AXS, Inc. Madison, WI, 1999.
11 G. M. Sheldrick, SHELXTL, an integrated system for solving, refining, and displaying crystal structures from diffraction data. Version 5.1. Bruker AXS, Inc. Madison, WI, 1998.
12 G. M. Sheldrick, SADABS, Empirical Absorption Correction Program, University of Göttingen, Göttingen, Germany, 1997.