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Organometallic chemistry in a conventional microwave oven: the facile synthesis of group 6 carbonyl complexes

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Abstract

Syntheses proceeding by reflux may be improved, accelerated and simplified, by carrying out the reaction in a modified conventional microwave oven. To demonstrate the potential of this method, the synthesis of over 20 group 6 organometallic compounds is reported. Hexacarbonyls, most notably $Mo(CO)_6$, react with a range of mono, and bi, and tridentate ligands in a modified conventional microwave oven. They generally proceed without an inert atmosphere, yields are high and reaction times are short. For example, *cis*-$[Mo(CO)_4(dppe)]$ is prepared in >95% yield in 20 min. Reaction of $Mo(CO)_6$ with dicyclopentadiene affords a simple one-step synthesis of $[CpMo(CO)_3]_2$ in >90% yield, which reacts further with alkynes in toluene to produce dimetallatetrahedrane derivatives, $[Cp_2Mo_2(CO)_4(\mu-RC_2R)]$; presumably *via* the in situ formation of air-sensitive $[CpMo(CO)_2]_2$. Dimolybdenum tetra-acetate is also prepared in 48% yield in 45 min, however, this reaction requires an inert atmosphere. While $W(CO)_6$ reacts rapidly with amines to give *cis* diamine adducts in high yields, direct reactions with phosphines are not so clean. Bis(phosphine) complexes are, however, cleanly formed when a small amount of piperidine is added to the reaction mixture, presumably *via* the bis(piperidine) complex *cis*-$[W(CO)_4(pip)_2]$. Reactions with $Cr(CO)_6$ generally require an inert atmosphere and proceed less cleanly, although the important synthon $[Cr(CO)_5Cl][NEt_4]$ was prepared in 30 min (74% yield), while $[(\eta^6-C_6H_5OMe)Cr(CO)_3]$ can be prepared in 45% after 4 h.
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1. Introduction

Over the past twenty years, the application of microwave irradiation towards the acceleration of a wide-range of organic and inorganic reactions, has received considerable attention [1–6]. The main benefit of this approach is one of a timesaving nature. More recently, however, a number of other interesting effects have been observed. Reactions generally carried out in toxic organic solvents may, under microwave irradiation, occur in water, thus allowing a greener approach [7], while the use of especially high boiling solvents with high dielectric loss tangents can negate the need for high pressures

in certain catalytic reactions [8]. Perhaps more impressively, recent work suggests that the enantioselectivity of certain reactions may be altered by microwave heating over the conventional thermal methods [9].

The microwave acceleration of organometallic reactions has been given relatively little attention, and in most examples reported to-date, Teflon autoclaves were utilized. Mingos and co-workers have reported the synthesis of rhodium and iridium(I) di-olefin complexes [10], $[Cp_2Rh]PF_6$ [10], $[(\eta^6-C_6H_6)Ru(\mu-Cl)]_2$ [10], $[IrCl(CO)(PPh_3)]$ [11] and $[RuCl(CO)(2,2'-bipy)_2]Cl$ [11], while Danks and co-workers have reduced 1-azabuta-1,3-diene iron tricarbonyl complexes with sodium borohydride [12], and prepared thiolate complexes, $[CpRu(dppm)(SR)]$, using a focused monomode microwave reactor [13]. Most importantly to this work, recently Green and co-workers have shown that group 6 metal carbonyls react with diamines and diphosphines

to give tetracarbonyl products, [M(CO)$_4$L] (L = en, bipy, dppm, dppe), with significant rate enhancements of the thermal reactions [14].

Carrying out microwave reactions in Teflon autoclaves requires specialist laboratory equipment and such closed systems present dangers due to the high pressures generated. Further, assigning the specific effect of microwave irradiation on the reaction acceleration *versus* a conventional open reflux system is difficult due to the major pressure and temperature differences between the two. In an open system, Mingos [15] and others [16–18] have clearly shown that the rate enhancement results from the coupling of solvents with high dielectric loss tangents with the microwave's irradiation, resulting in super-heating, thereby leading directly to reaction acceleration. This potential use of simple, safe and cost effective microwave-accelerated syntheses of organometallic complexes has hardly been explored.

Our interest in the microwave acceleration of organometallic reactions started following the realization that many important organometallic reactions are excluded from undergraduate laboratories by time constraints. For example, there is a wealth of metal carbonyl chemistry that is rarely explored at this level due to both the constraints of time and the need for an inert atmosphere (often due to the air-sensitivity of intermediate products). Thus in 1990, we first prepared the important synthon, *cis*-[Mo(CO)$_4$(pip)$_2$], in 80–90% yield over 30–40 min, and this was successfully turned into an undergraduate experiment, the details of which we have recently reported [19].

Over the past decade we have developed a range of microwave accelerated syntheses of group 6 carbonyl complexes, based predominantly on molybdenum but also including tungsten and chromium. All proceed in a modified conventional microwave oven at atmospheric pressure, and generally without need for an inert atmosphere. Prompted by the report of Green and co-workers [14], and the continuing interest in group 6 carbonyl chemistry both at a research and teaching level, we herein describe details of our successful synthetic procedures.

2. Results and discussion

In a conventional microwave oven, Mo(CO)$_6$ reacts smoothly with a range of mono- and bidentate amines and phosphines to give tetracarbonyl complexes in good to excellent yields (Fig. 1). With PPh$_3$, the final product is dependent upon the stoichiometry of the reaction; with one equivalent of phosphine, monosubstituted [Mo(CO)$_5$(PPh$_3$)] is isolated in 85% yield, along with a small amount (10%) of *trans*-[Mo(CO)$_4$(PPh$_3$)$_2$], which is the only product (70%) with two equivalents of phosphine. The *cis* isomer cannot be prepared directly in the microwave oven, but is readily isolated upon addition of PPh$_3$ to *cis*-[Mo(CO)$_4$(pip)$_2$] in refluxing dichloromethane. Microwave-accelerated syntheses of the tetracarbonyls, [Mo(CO)$_4$(bipy)], [Mo(CO)$_4$(dppm)] and [Mo(CO)$_4$(dppe)] in a closed system have previously been reported by Green and co-workers [14], reaction

Fig. 1. Microwave accelerated reactions of Mo(CO)$_6$.
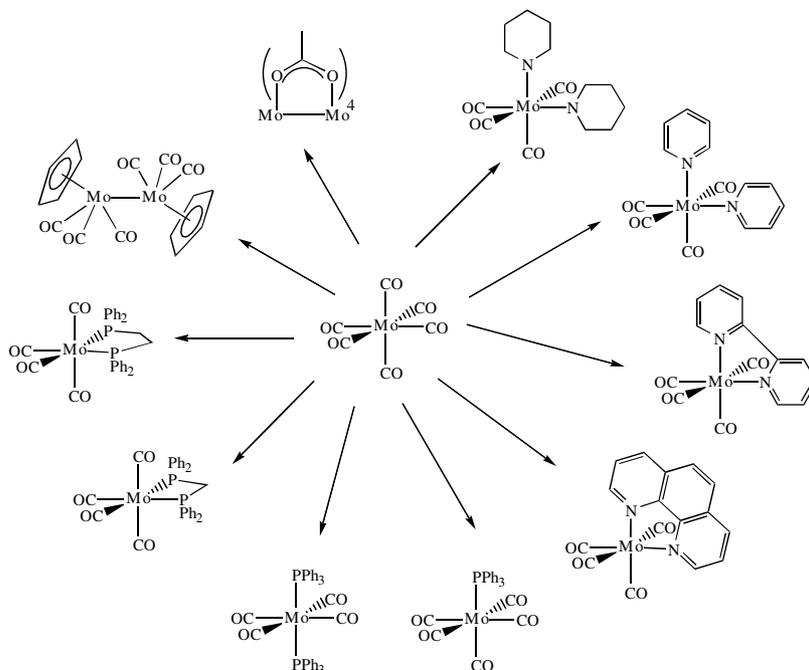
times being 30 s. While our synthetic procedure, as expected, takes longer (15–20 min) yields are higher for the diphosphine complexes and comparable for 2,2′-bipy.

The dimeric molybdenum(I) cyclopentadienyl complexes are important organometallic reagents and there are two syntheses of [CpMo(CO)$_3$]$_2$ in *Inorganic Synthesis* [20]. The first requires the preparation of sodium cyclopentadienide and it subsequent reaction with Mo(CO)$_6$ to give Na[CpMo(CO)$_3$], which is subsequently oxidised by iron(III) ammonium sulfate. In the second, the tris(acetonitrile) complex [Mo(CO)$_3$-(MeCN)$_3$] is first prepared, upon reflux of Mo(CO)$_6$ in acetonitrile for 4 h, and this is then reacted with freshly distilled cyclopentadiene at reflux for a further 2 h. While both routes offer high yields (89–98%) and can be scaled up to generate 40–80 g of product, they suffer from requiring a number of steps which must be carried out under an inert atmosphere and involve potentially hazardous reagents. An early synthesis of [CpMo(CO)$_3$]$_2$ involved the direct reaction of Mo(CO)$_6$ vapour and cyclopentadiene at 250 °C gave the desired product in 30% yield [21]. We have now found that in the microwave oven, *unpurified* dicyclopentadiene reacts with Mo(CO)$_6$ *in air* to give [CpMo(CO)$_3$]$_2$ in 94% yield after 1 h (Fig. 1) which is an important starting material for a wide-range of molybdenum chemistry.

In all the reactions described above an inert atmosphere is not necessary and, along with the timesaving, this makes these syntheses particularly appealing. Dimolybdenum tetra-acetate, [Mo$_2$(μ-O$_2$CMe)$_4$], is another important starting material in molybdenum

chemistry. Its synthesis typically involves heating Mo(CO)$_6$ and acetic acid for 20 h, in order to obtain a 37% yield [22]. In the absence of an inert atmosphere, all of our attempts to generate [Mo$_2$(μ-O$_2$CMe)$_4$] in the microwave failed. However, under argon, we were successful in getting a 48% yield with minimal work-up in just 45 min (Fig. 1). This then provides a simple, relatively high yielding, route to this important starting material in both research and undergraduate laboratories.

We have also explored the microwave-accelerated reactions of W(CO)$_6$ and to a lesser extent Cr(CO)$_6$ (Fig. 2). Simple amine derivatives of W(CO)$_6$ are easily prepared in a manner analogous to that described above for molybdenum, although yields are generally lower (35–85%) and reaction times longer (1–2 h). These differences are primarily due to the lower reactivity of W(CO)$_6$ *vs* Mo(CO)$_6$, however, the propensity of tungsten to undergo oxidation also lowers the yields since the reactions were carried out in air.

Direct reactions of phosphines with W(CO)$_6$ were very disappointing, large amounts of unreacted W(CO)$_6$ remaining even after 2 h at reflux. However, we were able to prepare [W(CO)$_4$(PPh$_3$)$_2$] and [W(CO)$_4$(dppm)] in 96% and 68% yield respectively and in just 20 min, simply by adding a few drops of piperidine to the reaction mixture. The exact role of the piperidine was not explored, but it seems logical that *cis*-[W(CO)$_4$(pip)$_2$] is initially formed and then the amines are replaced by the phosphine(s). This would also account for the mixture of *cis* and *trans* isomers of [W(CO)$_4$(PPh$_3$)$_2$] which is
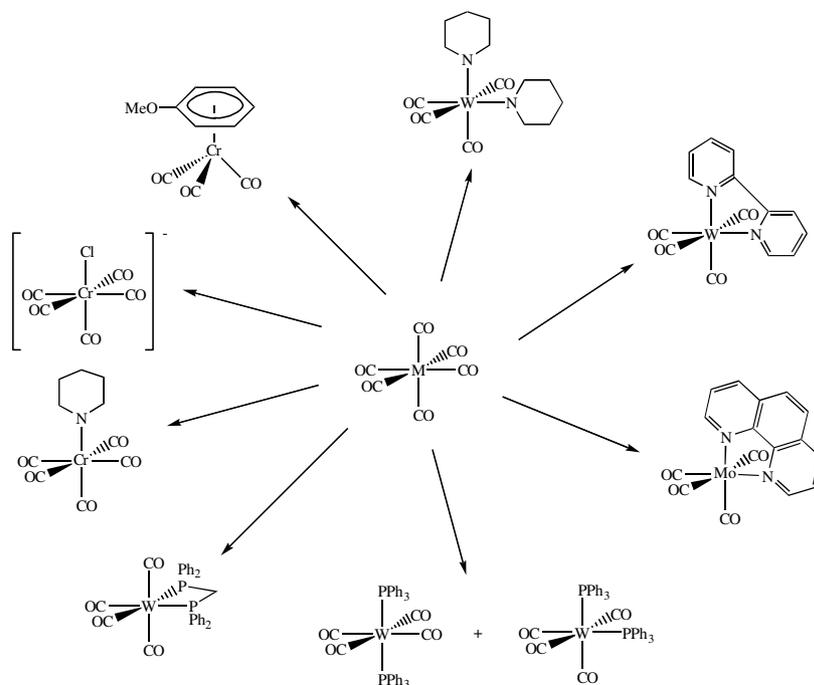

Fig. 2. Microwave accelerated reactions of Cr(CO)$_6$ and W(CO)$_6$.

formed. Further, as piperidine is released in the later step, the process is apparently catalytic, although again we have not fully explored this. Green and co-workers have prepared [W(CO)$_4$(dppm)], in comparable yields, directly from the diphosphine and W(CO)$_6$ *via* a microwave-accelerated process in a closed system [14]. It may be that the temperatures required for carbonyl substitution by a diphosphine are achievable under these conditions, but are not easily generated in the open system.

An attempt to prepare [CpW(CO)$_3$]$_2$ was not very successful. Heating W(CO)$_6$ and dicyclopentadiene for 90 min gave a brown solution from which small amounts only of the desired product were isolated after work-up and addition of piperidine had little effect to the reaction.

Reactions carried out with Cr(CO)$_6$ were of mixed success (Fig. 2). Under an argon atmosphere, reaction with NEt$_4$Cl proceeded smoothly to afford [Cr(CO)$_5$Cl][NEt$_4$] cleanly and in high yields (74%). The only reaction of Cr(CO)$_6$ to proceed in air was that with piperidine which yielded [Cr(CO)$_5$(pip)] after 40 min. The isolated yield of the latter was modest (15%), however, this is primarily due to the difficulty in separation from the diglyme.

Arene chromium tricarbonyl complexes have a wide range of applications and are important organometallic synthons. Reaction of Cr(CO)$_6$ with most arenes is, however, notoriously slow and requires high temperatures. Our initial experiments with mesitylene were disappointing, and while some reaction did occur, it was very slow and separation of the product from the diglyme and unreacted hexacarbonyl. Using anisole gave somewhat better results. Refluxing under an argon blanket for 4 h (against the 24 h reported in the literature) gave [(η^6-C$_6$H$_5$OMe)Cr(CO)$_3$] in 45% yield, and further work may be warranted in this area.

Microwave-accelerated organomolybdenum chemistry is not simply limited to the use of Mo(CO)$_6$ (Fig. 3). Diphosphine complexes [Mo(CO)$_4$(dppm)] and [Mo(CO)$_4$(dppe)] both react cleanly with more diphosphine to produce *cis*-[Mo(CO)$_2$(dppm)$_2$] and *cis*-[Mo(CO)$_2$-63%) over 40 min, and in this way the mixed diphos-

phine complex *cis*-[Mo(CO)$_2$(dppm)(dppe)] can also be formed (52%), shown to be the *cis* isomer by ^{31}P NMR spectroscopy. Dark brown *cis*-[Mo(CO)$_2$(bipy)$_2$] also results from [Mo(CO)$_4$(bipy)], although the reaction is slower (90 min).

As mentioned above, dimeric cyclopentadienyl molybdenum tricarbonyl complexes, [(η^5-C$_5$R$_5$)Mo-(CO)$_3$]$_2$, are important starting materials for a wide-range of organomolybdenum chemistry, in both high and low oxidation states. Much of this work involves the initial generation of the triply-bonded tetracarbonyl [(η^5-C$_5$R$_5$)Mo(CO)$_2$]$_2$, a transformation which requires high temperatures. For example, [CpMo(CO)$_2$]$_2$ is generated from [CpMo(CO)$_3$]$_2$ upon reflux in diglyme for 1.5–3 h while purging the solution with nitrogen. Our attempts to carry out this transformation in the microwave cavity under a static nitrogen atmosphere were not successful, possibly since the diglyme was not dry. However, we have successfully trapped this reactive intermediate in a number of cases. Thus, heating toluene solutions of [(η^5-C$_5$H$_4$R)Mo(CO)$_3$]$_2$ (R = H, Me, Bu^t) with a three-fold excess of PhC$_2$Ph for 2 h gave the dimetallatetrahedrane complexes [(η^5-C$_5$H$_4$R)$_2$Mo$_2$-(CO)$_4$(μ-PhC$_2$Ph)] in moderate yields (39–46%) after work-up (Fig. 3). In a similar fashion, thermolysis of [(η^5-C$_5$H$_4$Me)Mo(CO)$_3$]$_2$ and excess nitrobenzene in toluene for 1 h afforded a mixture of molybdenum(V) complexes [(η^5-C$_5$H$_4$Me)MoO(μ-NPh)]$_2$ and [(η^5-C$_5$H$_4$Me)$_2$Mo$_2$O$_2$(μ-NPh)(μ-O)], in yields comparable with those in the literature [23].

These experiments demonstrate that the unsaturated, air-sensitive, molybdenum–molybdenum triply bonded complexes, [(η^5-C$_5$H$_4$R)Mo(CO)$_2$]$_2$, can be prepared in air and reacted in situ in the microwave cavity. This allows some quite difficult chemistry to be carried out in an inexpensive and convenient manner. Further, the reactions proceed rapidly in toluene, a solvent with a low dielectric loss tangent and one, which while widely used in organometallic chemistry, is not usually associated with microwave-accelerated reactions.

In conclusion we have demonstrated the simple and often high yielding syntheses of a range of group 6 carbonyl complexes in a modified commercial micro-
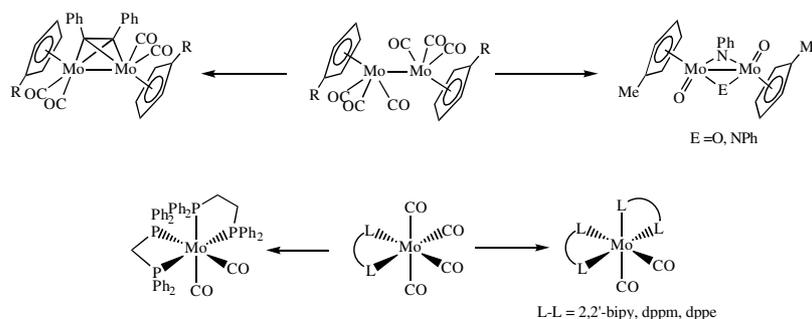

Fig. 3. Further microwave accelerated reactions of molybdenum carbonyls.

wave oven. The rate acceleration as compared to conventional methods allows many of these preparations to become the domain of the teaching laboratory, this being further enhanced by the negation in many instances of the need of an inert atmosphere. Microwave-enhanced reactions work best for $Mo(CO)_6$ in line with the established order of reactivity of the group 6 carbonyls; $Mo > W \sim Cr$ [34]. A further important advantage of the microwave-accelerated approach using group 6 hexacarbonyls is that in no instance was sublimation of the parent carbonyl a problem. This is often the case in conventional systems in which sublimation can lead to the blocking of the condenser, a potentially hazardous process.

3. Experimental

3.1. General

All reactions were carried out in a PROLINE *program 1250* 750 W microwave oven modified as shown. A hole bored in the top of the oven allowed connection of a water condenser to the reaction flask. Two holes bored in the side were fitted with a U-tube connected to a cold water supply. The rate of reflux could then be moderated by adjusting the volume of water in the cavity by moving the U-tube in or out. All reactions were carried out in air in a 100 ml round bottomed flask. A more detailed description of this apparatus has recently been published [18]. Solvents were used as supplied except for the toluene (distilled over sodium).

Chromatography was carried out on deactivated alumina (6% w/w distilled water) wet packed with light-petroleum. The solution to be separated was added to alumina (3–5 g) and the solvent removed under reduced pressure. The resulting solids were then deposited on top of the prepared column and separation effected by elution with progressively more polar solvents.

IR spectra were recorded on a Nicolet 205 FTIR spectrometer. NMR spectra were recorded on Bruker AMX400 and Avance500 spectrometers and internally referenced to residual solvent peaks (^{1}H, ^{13}C) or externally to $P(OMe)_3$ (^{31}P). Mass spectra were recorded on VG 7070 high resolution and VG Analytical ZAB2F spectrometers and elemental analyses were performed in house.

3.2. Syntheses

cis-[Mo(CO)$_4$(NHC$_5$H$_{10}$)$_2$] [24] – A diglyme (12.5 cm^3) and thf (5 cm^3) solution of $Mo(CO)_6$ (2.15 g, 8.14 mmol) and an excess of piperidine (5 cm^3) was heated for 40 min, which upon cooling lead to the deposition of a yellow crystalline solid. This was filtered, washed with hexane (2 × 10 cm^3) and air dried to yield

cis-[Mo(CO)$_4$(pip)$_2$] (2.54 g, 83%). IR(CH$_2$Cl$_2$): 2013m, 1934s, 1887vs, 1819s cm^{-1}.

[Mo(CO)$_4$(2,2'-bipy)] [25] – A diglyme (12.5 cm^3) and thf (5 cm^3) solution of $Mo(CO)_6$ (2.03 g, 7.69 mmol) and 2,2'-bipyridine (1.45 g, 9.28 mmol) was heated for 20 min to give a bright red precipitate. This was filtered, washed with hexane (2 × 10 cm^3) and air dried to yield [Mo(CO)$_4$(2,2'bipy)] (2.63 g, 94%). IR(CH$_2$Cl$_2$): 2015m, 1906vs, 1877s, 1831m cm^{-1}.

[Mo(CO)$_4$(1,10-phen)] [25] – A diglyme (15 cm^3) and thf (6 cm^3) solution of $Mo(CO)_6$ (2.00 g, 7.58 mmol) and 1,10-phenanthroline (3.01 g, 16.7 mmol) was heated for 15 min to give a bright red precipitate. This was filtered, washed with hexane (5 × 10 cm^3) and air dried to yield [Mo(CO)$_4$(1,10-phen)] (2.68 g, 91%) as a dark orange solid. IR(CH$_2$Cl$_2$): 2015s, 1905vs, 1877s, 1831m cm^{-1}.

cis-[Mo(CO)$_4$(py)$_2$] [26] – A diglyme (12.5 cm^3) and thf (5 cm^3) solution of $Mo(CO)_6$ (2.08 g, 7.91 mmol) and an excess of pyridine (3.6 cm^3) was heated for 20 min, affording a bright orange solution. Cooling in ice bath gave a yellow precipitate. This was filtered, washed with hexane (3 × 10 cm^3) and air dried to yield *cis*-[Mo(CO)$_4$(py)$_2$] (1.45 g, 50%). IR(CH$_2$Cl$_2$): 2014m, 1939s, 1893vs, 1832s cm^{-1}.

[Mo(CO)$_5$(PPh$_3$)] [27] – A diglyme (15 cm^3) and thf (6 cm^3) solution of $Mo(CO)_6$ (1.02 g, 3.86 mmol) and PPh$_3$ (1.23 g, 4.69 mmol) was heated for 40 min, which upon cooling in an ice bath lead to the deposition of a yellow precipitate. This was filtered, washed with hexane (3 × 10 cm^3) and air dried to yield *trans*-[Mo(CO)$_4$(PPh$_3$)$_2$] (0.29 g, 10%). Removal of thf and hexane from the washings under reduced pressure and further cooling of the remaining solution in an ice bath lead to the formation of a pale brown precipitate which was filtered washed with cold hexane (2 × 10 cm^3) and air dried to yield [Mo(CO)$_5$(PPh$_3$)] (1.62 g, 85%). IR(CH$_2$Cl$_2$): 2073s, 1946vs cm^{-1}.

trans-[Mo(CO)$_4$(PPh$_3$)$_2$] [27] – A diglyme (15 cm^3) and thf (6 cm^3) solution of $Mo(CO)_6$ (1.01 g, 3.83 mmol) and PPh$_3$ (2.39 g, 9.11 mmol) was heated for 80 min, and upon cooling in an ice bath lead to the deposition of a pale brown precipitate. This was filtered, washed with hexane (2 × 10 cm^3) and air dried to yield *trans*-[Mo(CO)$_4$(PPh$_3$)$_2$] (1.94 g, 70%). IR(CH$_2$Cl$_2$): 1953m, 1896vs cm^{-1}.

[Mo(CO)$_4$(dppm)] [28] – A diglyme (15 cm^3) and thf (6 cm^3) solution of $Mo(CO)_6$ (1.00 g, 3.78 mmol) and dppm (1.75 g, 4.56 mmol) was heated for 20 min. Upon cooling an orange precipitate resulted which was filtered, washed with hexane (2 × 10 cm^3) and air dried to yield [Mo(CO)$_4$(dppm)] (2.24 g, 87%). IR(CH$_2$Cl$_2$): 2022s, 1913vs, 1881s cm^{-1}.

[Mo(CO)$_4$(dppe)] [28] – A diglyme (15 cm^3) and thf (6 cm^3) solution of $Mo(CO)_6$ (1.00 g, 3.78 mmol) and dppe (1.81 g, 4.54 mmol) was heated for 20 min. Upon

cooling a yellow precipitate resulted which was filtered, washed with hexane (2×10 cm^3) and air dried to yield [Mo(CO)$_4$(dppe)] (2.19 g, 96%). IR(CH$_2$Cl$_2$): 2021s, 1911vs, 1884s cm^{-1}.

[CpMo(CO)$_3$]$_2$ [19] – A diglyme (25 cm^3) solution of Mo(CO)$_6$ (1.00 g, 3.78 mmol) and dicyclopentadiene (1 cm^3, 7.56 mmol) was heated for 1 h. The reaction mixture turned purple and was cooled in an ice bath. Distilled water (25 cm^3) was added to give a fine precipitate. Heating on a steam bath for 20 min resulted in aggregation of the precipitate and made filtration easier. The purple solid was filtered and washed with hexane (2×10 cm^3) and air dried to yield [CpMo(CO)$_3$]$_2$ (0.87 g, 94%). IR(CH$_2$Cl$_2$): 2014m, 1958vs, 1912s, 1900sh cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 5.31 (s, 10H).

[Mo$_2$(μ-O$_2$CMe)$_4$] [22] – Under an argon atmosphere, a diglyme (40 cm^3) solution of Mo(CO)$_6$ (1.00 g, 3.77 mmol) and acetic acid (1 cm^3) was heated for 45 min. After cooling to room temperature the bright yellow precipitate was filtered, washed with acetone (2×20 cm^3) and air dried to yield [Mo$_2$(μ-O$_2$CMe)$_4$] (0.39 g, 48%).

cis-[Mo(CO)$_2$(2,2′-bipy)$_2$] [29] – A diglyme (20 cm^3) solution of [Mo(CO)$_4$(2,2′-bipy)] (0.53 g, 1.46 mmol) and 2,2′-bipy (0.49 g, 3.13 mmol) was heated for 90 min. The reaction mixture turned black. Upon cooling a black-brown precipitate resulted, which was quickly filtered and washed thoroughly with hexane until the washings were no longer red. The remaining brown solid was air dried to yield *trans*-[Mo(CO)$_2$(2,2′-bipy)$_2$] (0.36 g, 53%). IR(KBr): 1776s, 1735s cm^{-1}.

cis-[Mo(CO)$_2$(dppm)$_2$] [29] – A diglyme (25 cm^3) solution of [Mo(CO)$_4$(dppm)] (1.00 g, 1.69 mmol) and dppm (0.78 g, 2.03 mmol) was heated for 40 min. Upon cooling in an ice bath a brown precipitate resulted which was filtered, washed with hexane (3×10 cm^3) and air dried to yield *cis*-[Mo(CO)$_2$(dppm)$_2$] (0.98 g, 63%) as a yellow powder. IR(CH$_2$Cl$_2$): 1859vs, 1790s cm^{-1}; ^{1}H NMR (acetone-d^6): δ 7.94–7.05 (m, 32H, Ph), 6.83 (t, J 7.4, 4H, Ph), 6.68 (t, J 7.3, 4H, Ph), 4.78 (m, 4H, CH$_2$); ^{31}P NMR (acetone-d^6) 18.3 (d, J 5.5), 2.3 (d, J 5.5).

cis-[Mo(CO)$_2$(dppe)$_2$] [29] – A diglyme (25 cm^3) solution of [Mo(CO)$_4$(dppe)] (1.00 g, 1.65 mmol) and dppe (0.78 g, 1.96 mmol) was heated for 40 min. Upon cooling in an ice bath a yellow precipitate resulted which was filtered, washed with hexane (3×10 cm^3) and air dried to yield *cis*-[Mo(CO)$_2$(dppe)$_2$] (0.83 g, 45%) as a yellow powder. IR(CH$_2$Cl$_2$): 1851vs, 1783s cm^{-1}; ^{1}H NMR (acetone-d^6): δ 7.81–7.05 (m, 36H, Ph), 6.83 (t, J 7.0, 2H, Ph), 6.21 (t, J 7.4, 2H, Ph), 3.49 (dd, J 40.1, 6.3, 4H, CH$_2$), 3.49 (dd, J 32.4, 5.3, 4H, CH$_2$); ^{31}P NMR (acetone-d^6) 67.3 (t, J 13.1), 47.2 (t, J 13.1).

cis-[Mo(CO)$_2$(dppm)(dppe)] – A diglyme (25 cm^3) solution of [Mo(CO)$_4$(dppm)] (0.80 g, 1.35 mmol) and dppe (0.65 g, 1.63 mmol) was heated for 40 min. Upon cooling in an ice bath a brown precipitate resulted which

was filtered, washed with hexane (3×10 cm^3) and air dried to yield *cis*-[Mo(CO)$_2$(dppm)(dppe)] (0.65 g, 52%) as a light yellow powder. IR(CH$_2$Cl$_2$): 1856vs, 1784s cm^{-1}; ^{1}H NMR (acetone-d^6): δ 8.08–6.93 (m, Ph, 28H), 6.85 (t, J 6.8, 2H, Ph), 6.83 (t, J 7.8, 2H, Ph), 6.48 (t, J 6.4, 2H, Ph), 6.40 (t, J 8.5, 2H, Ph), 6.29 (t, J 8.2, 2H, Ph), 6.21 (t, J 7.7, 2H, Ph), 4.82 (m, 1H, PCH$_2$P), 3.99 (dt, J 15.7, 8.6, 1H, PCH$_2$P), 3.53 (dd, J 33.0, 4.1, 2H, PCH$_2$CH$_2$P), 3.53 (dd, J 39.3, 5.0, 2H, PCH$_2$CH$_2$P); ^{31}P NMR (acetone-d^6): 71.2 (ddd, J 91, 26, 7), 55.2 (ddd, J 22, 18, 7), 17.4 (ddd, J 91, 26, 22), −1.8 (dt, J 26, 26, 18).

[Cp$_2$Mo$_2$(CO)$_4$(μ-PhC$_2$Ph)] [30] – A toluene (25 cm^3) solution of [CpMo(CO)$_3$]$_2$ (0.30 g, 0.61 mmol) and diphenylacetylene (0.33 g, 1.85 mmol) was heated for 2 h. The reaction mixture was cooled in an ice bath and filtered. The toluene was removed under reduced pressure and the remaining solid was washed with hexane (5×10 cm^3) and air dried to yield [Cp$_2$Mo$_2$(CO)$_4$(μ-PhC$_2$Ph)] (0.16 g, 39%) as a red solid. IR(CH$_2$Cl$_2$): 1988s, 1923vs, 1839s cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 7.23 (t, J 7.6, 4H, Ph), 7.10 (t, J 7.6, 2H, Ph), 7.06 (d, J 7.6, 4H, Ph), 5.18 (s, 10H, Cp).

[(η^5-C$_5$H$_4$Me)$_2$Mo$_2$(CO)$_4$(μ-PhC$_2$Ph)] [30] – A toluene (25 cm^3) solution of [(η^5-C$_5$H$_4$Me)Mo(CO)$_3$]$_2$ (0.30 g, 0.58 mmol) and diphenylacetylene (0.31 g, 1.74 mmol) was heated for 2 h. The reaction mixture was cooled in an ice bath and filtered. The toluene was removed under reduced pressure and the remaining solid was washed with hexane (5×10 cm^3) and air dried to yield [(η^5-C$_5$H$_4$Me)$_2$Mo$_2$(CO)$_4$(μ-PhC$_2$Ph)] (0.16 g, 40%) as a red solid. IR(CH$_2$Cl$_2$): 1982s, 1914vs, 1834s cm^{-1}.

[(η^5-C$_5$H$_4$Me)$_2$Mo$_2$O$_2$(μ-O)(μ-NPh)] and *[(η^5-C$_5$H$_4$Me)MoO(μ-NPh)]$_2$* [23] – A toluene (25 cm^3) solution of [(η^5-C$_5$H$_4$Me)Mo(CO)$_3$]$_2$ (1.00 g, 1.95 mmol) and nitrobenzene (0.50 cm^3) was heated for 1 h producing a dark yellow solution. The toluene was removed under reduced pressure and the solid was washed with hexane (2×10 cm^3). Chromatography was carried out. Eluting with light petroleum–dichloromethane (4:1) gave a yellow band which afforded [(η^5-C$_5$H$_4$Me)MoO(μ-NPh)]$_2$ (0.17 g, 18%), while eluting with light petroleum–dichloromethane (3:7) gave an orange band which afforded [(η^5-C$_5$H$_4$Me)$_2$Mo$_2$O$_2$(μ-O)(μ-NPh)] (0.09 g, 8%).

cis-[W(CO)$_4$(NHC$_5$H$_{10}$)$_2$] [26] – A diglyme (20 cm^3) and thf (5 cm^3) solution of W(CO)$_6$ (2.00 g, 5.68 mmol) and an excess of piperidine (5 cm^3) was heated for 2 h. A yellow precipitate was formed upon cooling which was filtered, washed with hexane (2×10 cm^3) and air dried to yield *cis*-[W(CO)$_4$(pip)$_2$] (0.93 g, 35%). IR(CH$_2$Cl$_2$): 2007m, 1923s, 1870vs, 1815s cm^{-1}.

[W(CO)$_4$(2,2′-bipy)] [27] – A diglyme (20 cm^3) and thf (5 cm^3) solution of W(CO)$_6$ (2.03 g, 5.77 mmol) and 2,2′-bipyridine (1.09 g, 6.98 mmol) was heated for 80 min to give a bright red precipitate. This was filtered,

washed with hexane (2×10 cm^3) and air dried to yield [W(CO)$_4$(2,2′bipy)] (1.02 g, 39%). IR(CH$_2$Cl$_2$): 2008m, 1976vs, 1893s, 1827m cm^{-1}.

[W(CO)$_4$(1,10-phen)] [27] – A diglyme (15 cm^3) and thf (6 cm^3) solution of W(CO)$_6$ (2.03 g, 5.77 mmol) and 1,10-phenanthroline (1.91 g, 10.6 mmol) was heated for 1 h to give a bright red precipitate. This was filtered, washed with hexane (5×10 cm^3) and air dried to yield [W(CO)$_4$(1,10-phen)] (2.33 g, 85%) as a dark orange solid. IR(CH$_2$Cl$_2$): 2008s, 1894vs, 1875s, 1827m cm^{-1}.

[W(CO)$_4$(PPh$_3$)$_2$] [27] – To a diglyme (25 cm^3) solution of W(CO)$_6$ (1.00 g, 2.84 mmol) and PPh$_3$ (1.81 g, 6.90 mmol) was added a few drops of piperidine. This was heated for 20 min. Upon cooling in an ice bath a yellow precipitate was deposited. This was filtered, washed with hexane (2×10 cm^3) and air dried to yield [W(CO)$_4$(PPh$_3$)$_2$] (2.23 g, 96%) as a mixture of *cis* and *trans* isomers. IR(CH$_2$Cl$_2$): 2018m, 1939m, 1907sh, 1889vs cm^{-1}.

[W(CO)$_4$(dppm)] [27] – To a diglyme (25 cm^3) solution of W(CO)$_6$ (1.00 g, 3.78 mmol) and dppm (1.31 g, 3.41 mmol) was added a few drops of piperidine. This was heated for 20 min. Upon cooling a yellow precipitate resulted which was filtered, washed with hexane (2×10 cm^3) and air dried to yield [W(CO)$_4$(dppm)] (1.32 g, 68%). IR(CH$_2$Cl$_2$): 2017s, 1904vs, 1874s cm^{-1}.

[Cr(CO)$_5$(NHC$_5$H$_{10}$)] [31] – A diglyme (12.5 cm^3) and thf (5 cm^3) solution of Cr(CO)$_6$ (1.00 g, 4.55 mmol) and an excess of piperidine (2.5 cm^3) was heated for 40 min. A green precipitate was formed upon cooling which was filtered, washed with hexane (2×10 cm^3) and air dried to yield [Cr(CO)$_5$(pip)] (0.18 g, 14%). IR(CH$_2$Cl$_2$): 2065m, 1929vs cm^{-1}.

[Cr(CO)$_5$Cl][NEt$_4$] [32] – Under a nitrogen atmosphere, a diglyme (20 cm^3) and thf (20 cm^3) solution of Cr(CO)$_6$ (4.00 g, 18.2 mmol) and Et$_4$NCl · H$_2$O (3.40 g, 18.5 mmol) was heated for 30 min. After cooling to room temperature bright yellow crystals were filtered off, washed with pentane (2×20 cm^3) and air dried to yield [Cr(CO)$_5$Cl][NEt$_4$] (4.80 g, 74%). IR(CH$_2$Cl$_2$) 2060s, 1926vs, 1854m cm^{-1}.

[(η^6-C$_6$H$_5$OMe)Cr(CO)$_3$] [33] – Under an argon atmosphere, a diglyme (20 cm^3) and thf (20 cm^3) solution of Cr(CO)$_6$ (1.00 g, 4.55 mmol) and anisole (2 cm^3) were refluxed for 4 h to yield a yellow solution. After filtration through Fuller's earth and removal of solvents and unreacted carbonyl under reduced pressure, extraction and crystallization from pentane afforded [(η^6-C$_6$H$_5$OMe)Cr(CO)$_3$] (0.50 g, 45%). IR(CH$_2$Cl$_2$) 1978m, 1906s cm^{-1}.

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