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# Studies directed toward the synthesis of chiral tungsten and molybdenum carbonyl complexes

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**Abstract**

A major challenge that must be met for an asymmetric intermolecular Pauson–Khand reaction is to be able to limit the possible positions on the metal complex for the organic partners. Toward this end, the synthesis of monometallic systems derived from $M(CO)_6$ and two bidentate ligands, in which the number of possible coordination sites is reduced to two, has been investigated.


*Keywords:* Pauson–Khand; Bidentate; Ligand; Electrodeficient; Chiral complexes; Molybdenum

## 1. Introduction

The preparation of well designed chiral metal carbonyl complexes with a limited number of coordination sites for use in asymmetric synthesis is a timely objective. A salient example of a transformation in which such complexes already find application is the Pauson–Khand reaction. This reaction, which unites an alkene, an alkyne, and carbon monoxide to form a cyclopentenone derivative, continues even after several decades to be the subject of considerable research [1], and provides still fertile ground for the development new chiral metal carbonyl complexes. It was our interest in the intermolecular version of this reaction that led us to study the preparation of novel chiral metal carbonyl complexes with a limited number of coordination sites, a study that produced unexpected, but interesting results, which are now reported.

The Pauson–Khand reaction is normally mediated by bimetallic complexes (Co–Co [1], Mo–Mo [2], Co–Mo [3], Co–W [4], Co–Rh [5], etc.), but it can also be performed with monometallic carbonyl complexes, such as those of metals from columns IV (Ti [6]), VI (Mo [7], W[8]), VIII (Fe [9], Ru [10]), and IX (Rh [11], Ir [12]). Various enantioselective versions of the Pauson–Khand reaction have been reported, most recently catalytic and with chiral ligands; however, to date, the only generally useful procedures are for intramolecular reactions. Intermolecular protocols that are enantioselective have been disclosed, but serve in part to underscore the difficulty in developing procedures that are truly efficient and general [13]. Moyano et al., for example, have nicely used non-symmetric bidentate ligands with $Co_2(CO)_8$ for intermolecular reactions, but to date have not been able to avoid the formation of diastereomers during their introduction, necessitating in most cases a separation [14]. The situation is rather comparable with monometallic and bimetallic complexes: several afford satisfactory results in the intramolecular version, but are not generally effective in the intermolecular.

A major challenge that needs to be met for an asymmetric intermolecular Pauson–Khand reaction is to be able to limit the possible positions on the complex for the organic partners. (In the case of the intramolecular reaction, the number of ultimate coordination sites is geometrically restricted because of the tethering of the double and triple bonds.) Toward this end, we decided to investigate the synthesis of monometallic systems derived from $M(CO)_6$ and two bidentate ligands [15], in which the number of possible

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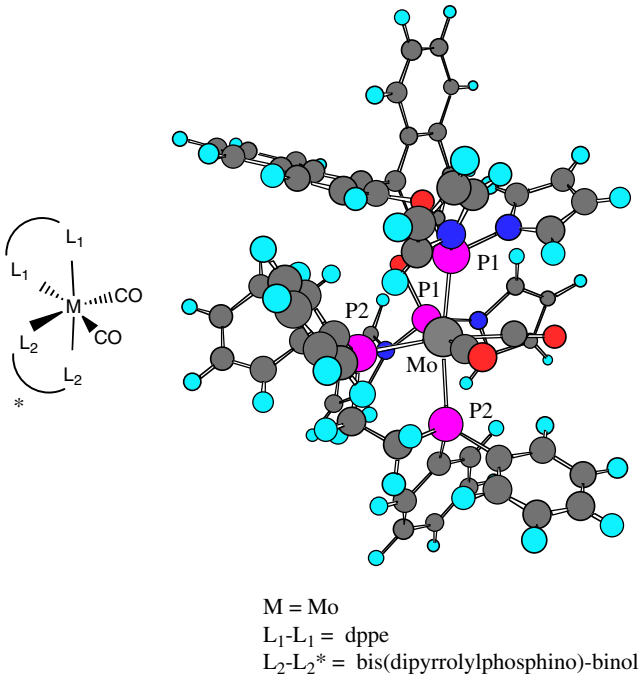



Fig. 1. Molecular modeling ($PM_3$) of a possible $M(CO)_2(L_1–L_1)(L_2–L_2)^*$ complex.

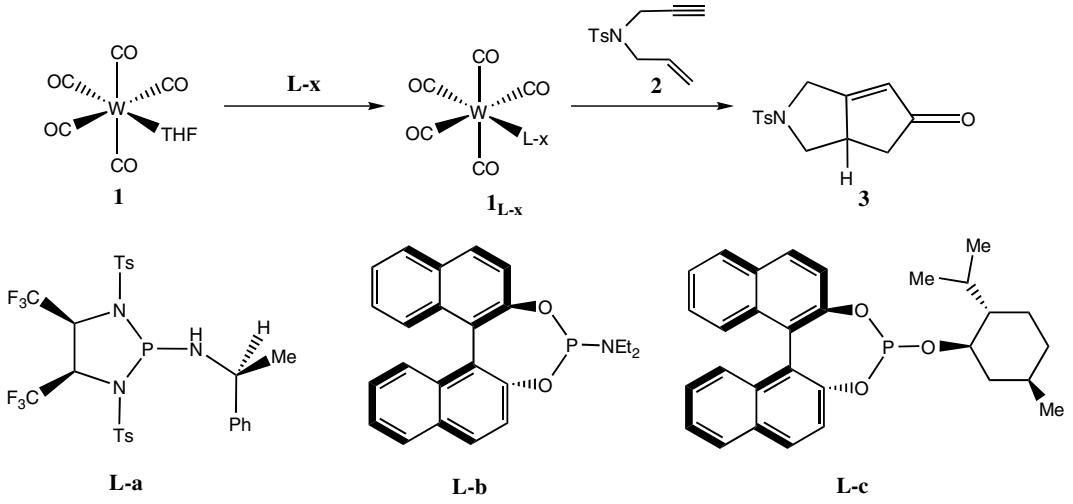
coordination sites would be reduced to two. Limiting the number of sites in this way and having chirality on one or both of the ligands appeared to offer an effective strategy for achieving enantioselective Pauson–Khand reactions. An example of a possible complex of this type is shown in Fig. 1. A successful approach along these lines would eliminate the loss of alkyne substrate occurring on separation of diastereomers, which seems to be nearly inevitable (for good enantioselectivity) when using bimetallic complexes with non-symmetric, and sometimes symmetric, ligands. With the envisaged strategy, in contrast, the diastereomeric complexes would first be separated, if necessary, and then allowed to react with the organic partners leading, hopefully, to a selective reaction.

## 2. Results and discussion

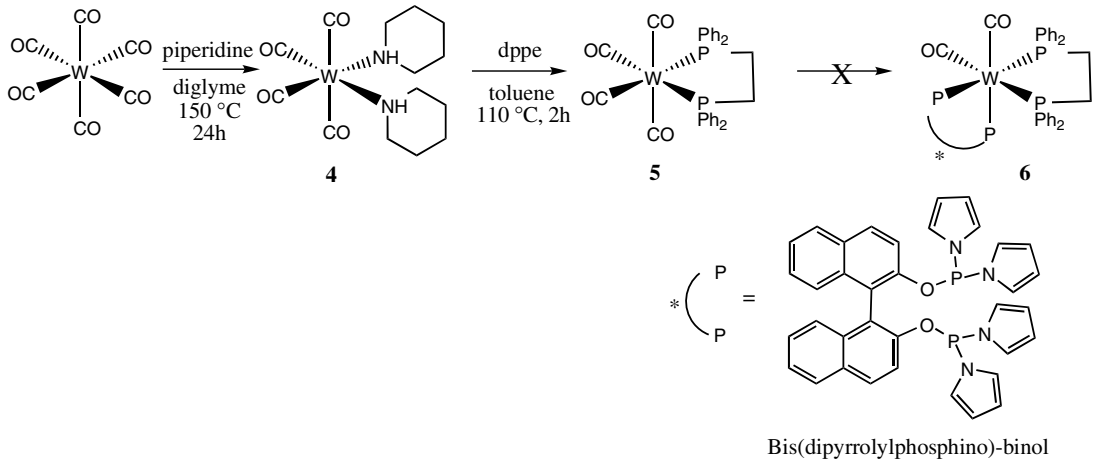
In an early example of the use of tungsten in the Pauson–Khand reaction, Hoye and Suriano [8] reported $W(CO)_5 \cdot THF$, obtained photochemically from $W(CO)_6$ in THF, to be an effective reaction mediator. We found that with chiral complexes derived from $W(CO)_5 \cdot THF$ and monophosphine ligands, the yields for an intramolecular reaction were good (58–63%), but the enantiomeric excesses, not surprisingly, turned out to be essentially nil (<2%). The bicyclization with 3 different tungsten complexes is shown in Scheme 1.

Thus, as previously surmised, a reduction in the number of possible coordination sites was required, which led us to study the introduction of 2 different bidentate ligands; however, the introduced bidentate ligands could not be coplanar (*mer* isomer), for this would make the subsequent Pauson–Khand reaction geometrically impossible (axial disposition of the remaining coordination sites). Few examples, though, of selective ligand introduction in a bidendate-coordinated carbonyl complex have been described in the literature [16]. A possible means to control the regiochemistry of the insertion of the second bidentate ligand might be to introduce initially an electron-rich bidentate ligand, which would result in a relative labilization of the cis positions (“cis labilization effect” [17]), but this strategy has possible pitfalls [18].

In an initial test of this approach, it was planned that bis(diphenylphosphino)ethane (dppe) would be introduced first, followed by an electron-poor binol derivative having on each oxygen a dipyrrolylphosphino group (Scheme 2). The dppe complex **5** could be conveniently prepared in 77% yield from the stable intermediate **4** by using the procedure described by Darensbourg and Kump [19] but, unfortunately, the introduction of the binol derivative proved to be impossible. This failure is probably the consequence of both the electron donating properties of dppe, which makes all of the CO ligands less labile [20], and



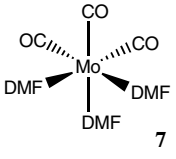

Scheme 1.




Scheme 2.

the electrodeficient character of the phosphorus atoms in the binol derivative.

In order to overcome this problem of reactivity, it was decided that the generally more reactive molybdenum complexes should be examined in place of the tungsten complexes. In 2005, Carretero et al. reported a Pauson–Khand reaction using $Mo(CO)_3(DMF)_3$ (**7**), which was found to be reactive under mild conditions [7c]. Relevant to the present work, the X-ray structure of this complex showed that it was the *fac* isomer (Fig. 2) [21]. Thus, starting from $Mo(CO)_3(DMF)_3$, it appeared that it could be possible to control the introduction of the bidentate ligands: the first bidentate ligand would undoubtedly displace two of the DMF ligands, whereupon the next group displaced could be expected to be the remaining DMF to yield ultimately the diastereomeric *fac*-$[Mo(CO)_2(L_1–L_1)(L_2–L_2)^*]$ complexes (Scheme 3).

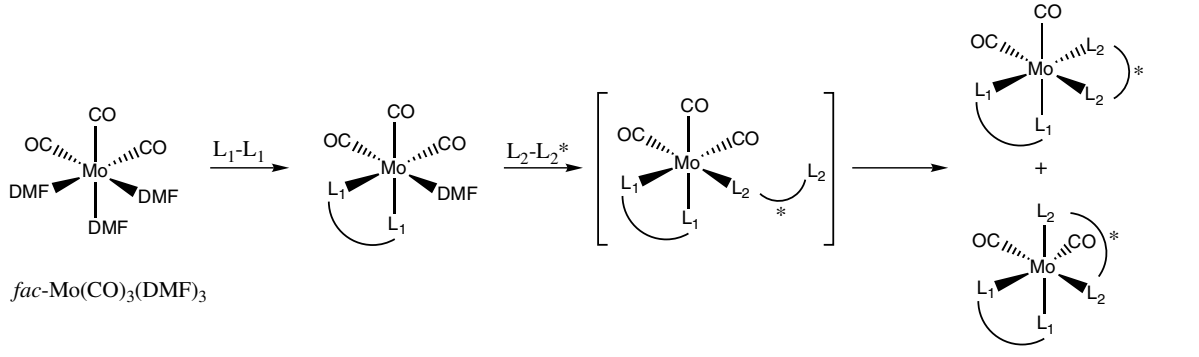



*fac*-$[Mo(CO)_3(DMF)_3]$

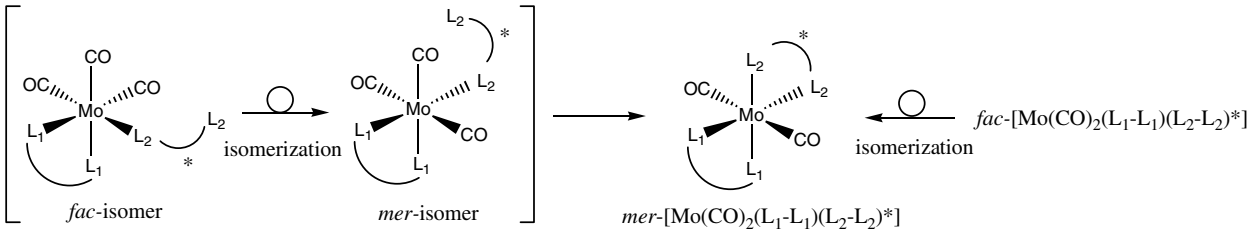
Fig. 2. *Fac* disposition of DMF ligands in complex **7**.

However, while the *fac* isomer $M(CO)_3L_3$ in brackets is electronically favored because of Mo to CO back-donation, the *mer*-isomer should be preferred sterically. Thus, conceivably, a *fac* to *mer* isomerization involving migration of the first $L_2$ (or an $L_1$) might take place through L and CO interchange prior to the final Mo–$L_2$ bond formation. This isomerization, though, could also occur in the final *fac*-isomers $Mo(CO)_2(L_1–L_1)(L_2–L_2)^*$ (Scheme 4).

Isomerizations of this kind are well precedented. Rousche and Dobson [22] observed a migration of a monodentate ligand, through dissociation–association, on heating *fac*-$[Mo(CO)_3(\eta^2\text{-dppe})\{P(OPr^i)_3\}]$ at 120 °C to give *mer*-$[Mo(CO)_3(\eta^2\text{-dppe})\{P(OPr^i)_3\}]$. The same research group [23] has also described the isomerization of *fac*-$[Mo(CO)_3(\eta^2\text{-dppe})(PPh_3)]$ at 125 °C (but, in contrast, *fac*-$[Mo(CO)_3(\eta^2\text{-dppe})(C_6H_{11}NH_2)]$ was found to be stable even at elevated temperatures). Darensbourg et al. [24] observed that *fac*-$[W(CO)_3(^{13}CO)(\eta^2\text{-dppe})]$ undergoes thermal transformation to a mixture of facial and meridional




Scheme 3.

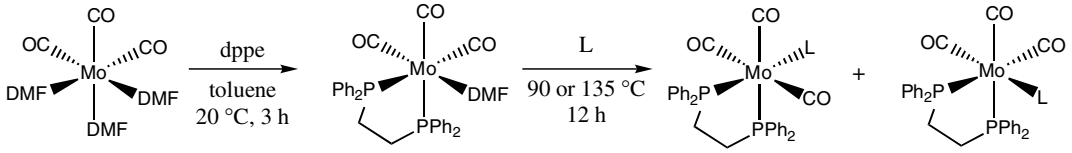



Scheme 4.

isomers, as later seen with $[W(CO)_3(\eta^2\text{-diphos})(\eta^1\text{-diphos}')]$ (diphos = diphosphine ligand) by Hsu and Yeh [25]. More recently, Fukumoto and Nakazawa[26] have demonstrated the ability of silanes to catalyze *fac* to *mer* isomerization in *fac*-$[Mo(CO)_3\{P(OR)_3\}_3]$. Interestingly, Schenk and Hilpert[27] described a switching of ligands, but without isomerization, on heating the four-membered chelate *fac*-$[Mo(CO)_3(\eta^2\text{-dppm})(NCMe)]$ and dppe to afford the more stable five-membered chelate *fac*-$[Mo(CO)_3(\eta^2\text{-dppe})(\eta^1\text{-dppm})]$; in contrast, Krishnamurthy et al. reported that treatment of *fac*-$[Mo(CO)_3(NCMe)\{\eta^2\text{-}Ph_2PN(Pr^i)PPh(dmpz)\}]$ (dmpz = 3,5-dimethylpyrazol-1-yl) with dppe produced both *fac*- and *mer*-$[Mo(CO)_3\{\eta^2\text{-}Ph_2PN(Pr^i)PPh(dmpz)\}(\eta^1\text{-dppe})]$, in which the four-membered diphosphazane ring remains intact and the dppe is coordinated in an $\eta^1$-fashion [28]. What distills from the ensemble of this work is that predictions of stereochemistry in these systems can be quite hazardous. In light of this, we prudently began our work on this approach by introducing first dppe in *fac*-$[Mo(CO)_3(DMF)_3]$ (**7**) and then different monophosphorus ligands (triphenyl phosphite, triethyl phosphite, and tripyrrolylphosphine) in the resulting complex. These experiments, together with an X-ray structure of *mer*-$[Mo(CO)_3(dppe)(P(pyrrolyl)_3)]$ (*mer*-**9c**), are shown in Scheme 5.

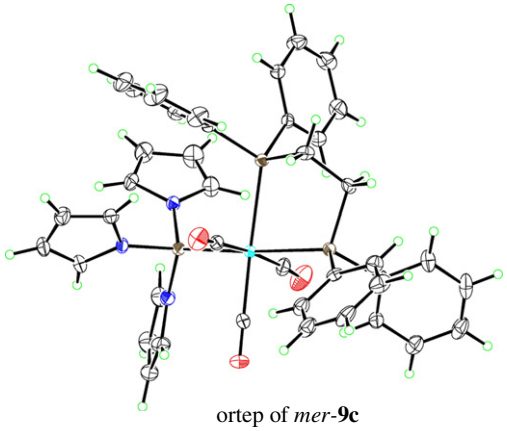
Both the facial and meridional isomers were generally formed, but in different ratios at a given temperature. For example, at 90 °C triphenyl phosphite produced an equimolar mixture of the two isomers, while triethyl phosphite afforded mainly the *fac* and tripyrrolylphosphine mostly the *mer*. Not surprisingly, when the reactions were performed at 135 °C, the *mer* isomers were formed preferentially with all three ligands. With tripyrrolylphosphine, the *mer* isomer was produced exclusively. The $^{31}P$ NMR displayed for $P(pyrrolyl)_3$ one signal at 135.4 ppm (dd, $^2J_{P-Pcis} = 27$ Hz, $^2J_{P-Ptrans} = 119$ Hz) for this isomer (one signal at 128.2 ppm (t, $^2J_{P-Pcis} = 32$ Hz) for the *fac* derivative) [29]. The *mer* isomers would seem to suffer fewer severe steric interactions, which could explain most of these results; however, electronic factors may also be involved.

The investigation was continued with the bidentate ligand bis(dipyrrolylphosphino)-binol, the hope being that after the formation of the first P–Mo bond, the subsequent P–Mo bond formation leading to chelation would be faster




**7** *fac*-$[Mo(CO)_3(DMF)_3]$ **8** *fac*-$[Mo(CO)_3(\eta^2\text{-dppe})(DMF)]$ *mer*-**9 a-c** *fac*-**9 a-c**

| L | temperature (°C) | yield(%) | *mer*-**9**/*fac*-**9** |
|---|---|---|---|
| **a** $P(OPh)_3$ | 90 | 77 | 50/50 |
| | 135 | 78 | 90/10 |
| **b** $P(OEt)_3$ | 90 | 85 | 5/95 |
| | 135 | 85 | 70/30 |
| **c** $P(pyrrolyl)_3$ | 90 | 70 | 80/20 |
| | 135 | 71 | 100/0 |



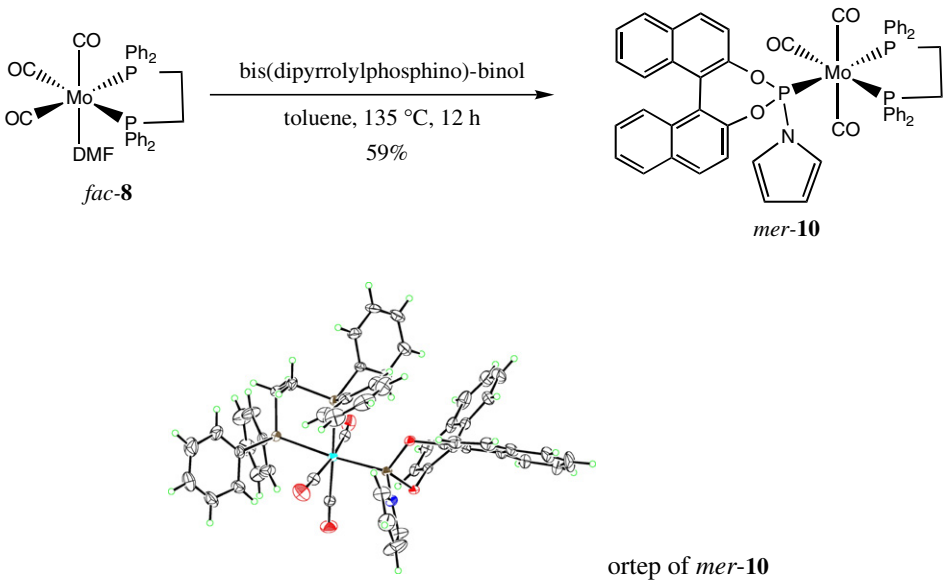
ortep of *mer*-**9c**

Scheme 5.

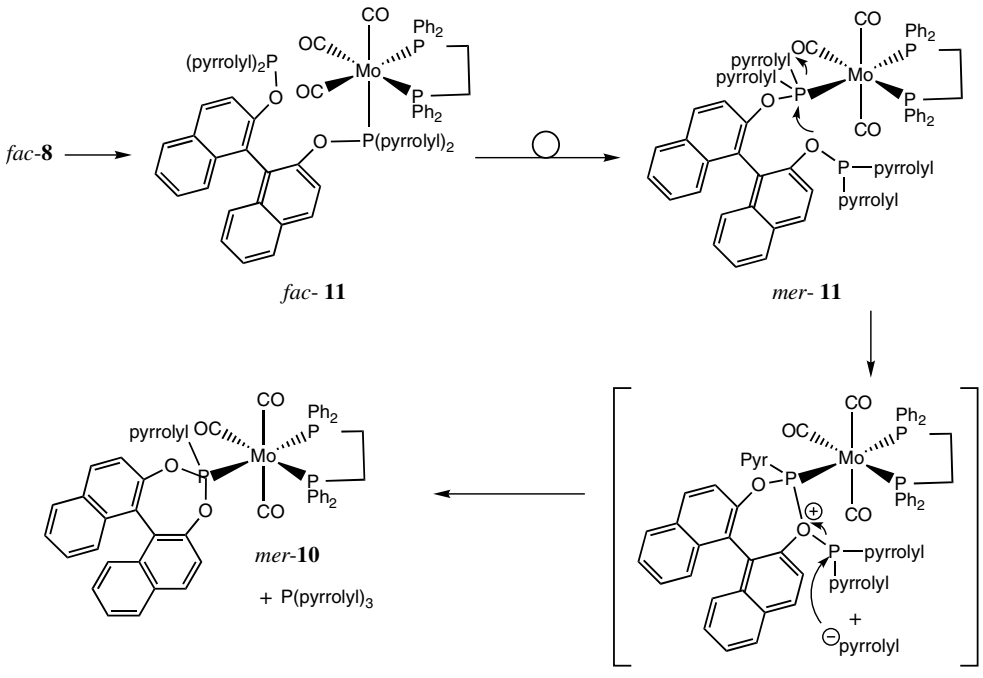
than any *fac* to *mer* P–CO rearrangement and that the product would be stable to isomerization. The reaction of *fac*-**8** with the bis(dipyrrolylphosphino)-binol ligand for 12 h at 135 °C (at 90 °C, the reaction was extremely slow) led, however, to a totally unexpected complex, *mer*-**10** (Scheme 6).

Again unexpectedly, the complex *mer*-**10** was also obtained starting from *fac*-[$Mo(CO)_3\{\eta^2$-bis(dipyrrolylphosphino)-binol}(DMF)] and dppe. The bis(dipyrrolylphosphino)-binol ligand itself is stable in toluene at 135 °C for 12 h ($^{31}P$ NMR: unique singlet at 108.3 ppm), as is the [$Mo(CO)_4$(bis(dipyrrolylphosphino)-binol)] complex [30] ($^{31}P$ NMR: unique singlet at 147.6 ppm). Thus, the unexpected events must begin with the introduction of the second bidentate ligand. In Scheme 7, we show a plausible pathway to explain the formation of *mer*-**10** from *fac*-**8**.

Isomerizations analogous to that of *fac*-**11** to *mer*-**11** have previously been observed (see above), but the subsequent steps are, to the best of our knowledge,




Scheme 6.




Scheme 7.

unprecedented. It is possible, though, that loss of P(pyrrolyl)$_3$ occurs prior to *fac* to *mer* isomerization. We have never observed the formation of any **9c** in the reaction; however, the free ligand has been identified in the crude mixture by $^{31}$P NMR (78.4 ppm). Finally, the leaving group ability of the phosphorus substituant is important [31], which is consistent with the proposed pathway.

## 3. Conclusion

It has been shown in this initial study that introduction of a second bidentate ligand in a molybdenum tetracarbonyl complex is fraught with complications, inter alia *fac* to *mer* isomerism and unprecedented ligand fragmentation. However, the preparation of enantiopure molybdenum carbonyl complexes, with only 2 available sites for coordination, for use in asymmetric synthesis warrants further study.

## 4. Experimental

Thin-layer chromatography was performed on (0.2 mm) silica sheets, which were visualized under ultraviolet light and by heating the plate after treatment with phosphomolybdic acid in ethanol, a *p*-anisaldehyde staining solution (80 mL of 95% ethanol, 2.9 mL of sulfuric acid, 0.86 mL of acetic acid, 2.1 mL of *p*-anisaldehyde), nihydrin in ethanol, ceric ammonium molybdate in ethanol, or basic, aqueous $KMnO_4$. Silica gel (0.040–0.063 mm) was employed for flash column chromatography. Melting points were obtained on a Buchi melting point apparatus and are uncorrected. A Nicolet Impact 400 infrared spectrometer was used to record IR spectra. NMR spectra were recorded on a Bruker AV 300 apparatus and are reported in ppm. Mass spectra were recorded using an Esquire 3000 Bruker spectrometer (ESI mode). Microanalyses were performed by the analytical service of the DCM. Toluene and tetrahydrofuran were distilled from sodium-benzophenone, triethylamine and pyrrole from $CaH_2$, and dimethylformamide from BaO prior to use. All solvents were degassed before reactions, which were carried out under argon. $W(CO)_6$ and $Mo(CO)_6$ were purchased from Acros Organics. The complexes $W(CO)_5 \cdot THF$ [8], $W(CO)_4$(piperidine)$_2$ [19], $W(CO)_4$dppe [19], $Mo(CO)_4$(piperidine)$_2$ [19], and $Mo(CO)_3(DMF)_3$ [7c] and chlorodipyrrolylphosphine [32], menthyl phosphorodichloridite, and the binol ligands[33] were synthesized through literature procedures.

### 4.1. Preparation of $W(CO)_5$ complex $\mathbf{1}_{\mathbf{L\text{-}a}}$

A solution of *meso*-1,1,1,4,4,4-hexafluoro-$N^2$,$N^3$-ditosylbutane-2,3-diamine [34] (0.252 g, 0.50 mmol) in 2.0 mL of THF was cooled to −78 °C under argon and 0.68 mL of a solution of *n*-BuLi (1.6 M in hexane, 1.1 mmol) was added dropwise. The mixture was stirred at −78 °C for 30 min and then allowed to warm to 20 °C. After 2 h, the resulting dark brown mixture was cooled to −78 °C, $PCl_3$ (0.090 mL, 1.03 mmol) was added slowly, and the temperature was allowed to rise to 20 °C over 2 h. The mixture was then cooled again to −78 °C and (*S*)-α-methylbenzylamine (0.210 mL, 1.63 mmol) was added dropwise. After 2 h, the mixture was allowed to warm to 20 °C and was then stirred overnight. The solvent was removed under reduced pressure and the residue was taken up in toluene/EtOAc (95/5), which was filtered though a thin pad of silica gel to remove the amine salt. The filtrate was then concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel, eluting first with 5% ethyl acetate in pentane and then with 5% ethyl acetate in toluene, to afford (1*S*)-*N*-(*meso*-4,5-bis(trifluoromethyl)-1,3-ditosyl-1,3,2-diazaphospholidin-2-yl)-1-phenylethanamine (**L-a**, 0.140 g with 0.056 g of recovered starting material, 55% yield) as a colorless oil: $^{31}$P NMR (121.49 MHz, $CDCl_3$) $\delta$ 102.86; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 1.64 (d, $J = 6.8$ Hz, 3H), 2.40 (s, 3H), 2.46 (s, 3H), 3.88 (t, $J = 10$ Hz, 1H), 4.06–4.26 (m, 2H), 4.61–4.74 (m, 1H), 7.13 (d, $J = 8.0$ Hz, 2H), 7.30–7.38 (m, 7H), 7.51 (d, $J = 8.3$ Hz, 2H), 7.75 (d, $J = 8.2$ Hz, 2H); $^{19}$F NMR (282.4 MHz, $CDCl_3$) $\delta$ −66.23 to −66.34 (m, 3F), −66.48 to −66.58 (m, 3F).

A solution of $W(CO)_5 \cdot THF$ in THF [8] (27 mL, ca. 1.8 mmol) was added to amine derivative **L-a** (0.480 g, 0.73 mmol) in 4 mL of THF under argon, and the resultant mixture was stirred at 20 °C overnight. The solvent was then removed by rotary evaporation and the excess tungsten reagent was eliminated at 45 °C under high vacuum. The residue was dissolved in dichloromethane, which was filtered. The filtrate was concentrated to afford 0.620 g (86%) of complex $\mathbf{1}_{\mathbf{L\text{-}a}}$: $^{31}$P NMR (121.49 MHz, $CDCl_3$) $\delta$ 102.75 ($^1J_{183W-31P} = 368$ Hz); $^1$H NMR (300 MHz, acetone-$d_6$) $\delta$ 1.67 (d, $J = 6.6$ Hz, 3H), 2.46 (s, 3H), 2.50 (s, 3H), 4.47–4.52 (m, 2H), 4.62–4.73 (m, 2H), 7.27–7.81 (m, 13H); $^{19}$F NMR (282.4 MHz, $CDCl_3$) $\delta$ −112.38 to −112.31 (m, 3F), −111.95 to −111.88 (m, 3F); IR 2081, 1948 cm$^{-1}$.

### 4.2. Preparation of $W(CO)_5$ complex $\mathbf{1}_{\mathbf{L\text{-}b}}$

A solution of $W(CO)_5 \cdot THF$ in THF [8] (75 mL, ca. 2.8 mmol) was added to a solution of the (*R*)-binol phosphoramidite ligand (**L-b**) (0.324 g, 0.84 mmol) in 5 mL of THF and the resultant mixture was stirred at 60 °C for 2. The solvent was then removed under reduced pressure and the excess tungsten reagent was eliminated at 75 °C under high vacuum. The residue was subjected to flash chromatography on silica gel with 10% ethyl acetate in pentane to afford the tungsten pentacarbonyl complex $\mathbf{1}_{\mathbf{L\text{-}b}}$ (0.483 g, 81%): mp 148–151 °C (dec); $^{31}$P NMR (121.49 MHz, $CDCl_3$) $\delta$ 159.2 ($^1J_{183W-31P} = 379$ Hz); $^1$H NMR (300 MHz) $\delta$ 1.02 (m, 6H), 2.83 (m, 2H), 3.13 (m, 2H), 7.0–7.4 (m, 8H), 7.59 (d, $J = 6.0$ Hz, 1H), 7.83 (m, 2H), 7.94 (d, $J = 8.0$ Hz, 1H); IR ($CH_2Cl_2$) 2076, 1984, 1938 cm$^{-1}$; MS (ESI$^+$) *m*/*z* 712 [M+H]$^+$ (100%). Anal.

Calc. for $C_{29}H_{22}NO_7PW$: C, 48.97; H, 3.12; N, 1.97. Found: C, 49.29; H, 3.11; N, 2.01%.

### 4.3. Preparation of $W(CO)_5$ complex $\mathbf{1_{L\text{-}c}}$

A solution of $W(CO)_5 \cdot THF$ in THF [8] (75 mL, ca. 2.8 mmol) was added to a solution of the (*R*)-binol (*1R,2S,5R*)-menthol phosphite ligand (**L-c**) (0.432 g, 0.92 mmol) in 5 mL of THF and the resultant mixture was stirred at 60 °C for 2 h. The solvent was then removed under reduced pressure and the excess tungsten reagent was eliminated at 75 °C under high vacuum. The residue was subjected to flash chromatography on silica gel with 10% ethyl acetate in pentane to afford the tungsten pentacarbonyl complex $\mathbf{1_{L\text{-}c}}$ (0.525 g, 72%): mp 172–174 °C (dec); $^{31}P$ NMR (121.49 MHz, $CDCl_3$) $\delta$ 149.3 ($^1J_{183W-31P}$ = 407 Hz); $^1H$ NMR (300 MHz) $\delta$ 0.40 (d, $J$ = 6.9 Hz, 3H), 0.70 (d, $J$ = 7.0 Hz, 3H), 0.80 (m, 4H), 1.20 (m, 4H), 1.50 (m, 2H), 1.85 (m, 1H), 2.15 (m, 1H), 4.20 (br s, 1H), 7.18 (m, 4H), 7.36 (m, 2H), 7.54 (d, $J$ = 8.0 Hz, 1H), 7.87 (m, 4H), 7.95 (d, $J$ = 6.0 Hz, 1H); IR($CH_2Cl_2$) 2078, 1991, 1935 $cm^{-1}$; MS ($ESI^+$) *m/z* 817 $[M+Na]^+$ (100%). Anal. Calc. for $C_{35}H_{30}O_8PW$: C, 52.98; H, 3.81. Found: C, 53.15; H, 3.93%.

### 4.4. Preparation of fac-mer-9a–c. Representative procedure (9b)

A stirred solution of freshly prepared $Mo(CO)_3(DMF)_3$ (0.600 g, 1.50 mmol) and bis(diphenylphosphino)ethane (0.598 g, 1.50 mmol) in 25 mL of dry toluene–DMF (4:1) was stirred at 20 °C for 3 h. Triethyl phosphite (0.257 mL, 1.50 mmol) in 5 mL of toluene was then added and the reaction mixture was heated at 90 °C for 12 h. After being allowed to cool to 20 °C, the reaction mixture was filtered through a pad of celite and the filtrate was concentrated under reduced pressure to give the crude product (95:5, *fac*:*mer*, by $^{31}P$ NMR). Purification of this material was accomplished by flash chromatography on silica gel with 20% ethyl acetate in pentane to give the more polar complex, *fac*-**9b** (0.903 g, 81%): mp 209–212 °C (dec); $^{31}P$ NMR (121.49 MHz, $CDCl_3$) $\delta$ 156.6 (t, $^2J_{P-Pcis}$ = 41 Hz, 1 P), 52.7 (br s, 2P); $^1H$ NMR (300 MHz) $\delta$ 1.89 (m, 9H), 2.48 (m, 2H), 2.84 (m, 2H), 3.38 (m, 6H), 7.27 (s, 12H), 7.55 (s, 4H), 7.68 (s, 4H); IR ($CH_2Cl_2$) 1937, 1848, 1826 $cm^{-1}$; MS ($ESI^+$) *m/z* 769 $[M + Na]^+$ (86%), 747 $[M+H]^+$ (100%).

The reaction was repeated, but at 135 °C, and the crude product (70:30, *mer*:*fac*, by $^{31}P$ NMR) was purified by flash chromatography on silica gel with 20% ethyl acetate in pentane to give the more less polar complex, *mer*-**9b** (0.669 g, 60%): mp 215–218 °C (dec); $^{31}P$ NMR (121.49 MHz, $CDCl_3$) $\delta$ 176.2 (dd, $^2J_{P-Pcis}$ = 24 Hz, $^2J_{P-Ptrans}$ = 134 Hz, 1 P), 62.7 (d, $^2J_{P-Ptrans}$ = 134 Hz, 1 P), 53.4 (s, 1P); $^1H$ NMR (300 MHz) $\delta$ 1.12 (t, $J$ = 5.6 Hz, 9 H), 2.39 (br s, 2H), 2.45 (bs, 2H), 3.90 (q, $J$ = 5.6 Hz, 6H), 7.34 (s, 12H), 7.59 (m, 8H); IR ($CH_2Cl_2$) 2075, 2023, 1974, 1944, 1858 $cm^{-1}$. Anal. Calc. for $C_{35}H_{39}O_6P_3Mo$: C, 56.47; H, 5.28. Found: C, 56.61; H, 5.26%.

Complexes **9a** (at 90 °C, 77% combined yield; at 135 °C, 78% combined yield) and **9c** (at 90 °C, 70% combined yield; at 135 °C, 71% combined yield) were prepared in the same manner. *fac*-**9a**: $^{31}P$ NMR (121.49 MHz, $CDCl_3$) $\delta$ 145.0 (t, $^2J_{P-Pcis}$ = 35 Hz, 1P), 52.3 (br s, 2P);*mer*-**9a**. $^{31}P$ NMR (121.49 MHz, $CDCl_3$) $\delta$ 164.9 (dd, $^2J_{P-Pcis}$ = 31 Hz, $^2J_{P-Ptrans}$ 141 Hz, 1P), 62.4 (d, $^2J_{P-Ptrans}$ = 141 Hz, 1P), 53.4 (s, 1P); MS ($ESI^+$) *m/z* 889 $[M+H]^+$ (20%), 415 (100%). *fac*-**9c**: $^{31}P$ NMR (121.49 MHz, $CDCl_3$) $\delta$ 128.2 (t, $^2J_{P-Pcis}$ = 32 Hz, 1P), 52.4 (br s, 2P); $^1H$ NMR (300 MHz) $\delta$ 1.39 (s, 2H), 2.48 (s, 2H), 6.12 (s, 6H), 6.31 (s, 6H), 7.19-7.39 (m, 16H), 7.72 (m, 4H); IR ($CH_2Cl_2$) 2014, 1949, 1896, 1868 $cm^{-1}$. *mer*-**9c**: mp 220–224 °C (dec); $^{31}P$ NMR (121.49 MHz, $CDCl_3$) $\delta$ 135.4 (dd, $^2J_{P-Pcis}$ = 27 Hz, $^2J_{P-Ptrans}$ = 119 Hz, 1P), 60.9 (d, P, $^2J_{P-Ptrans}$ = 119 Hz, 1P), 52.9 (s, 1P); $^1H$ NMR (300 MHz) $\delta$ 1.38 (s, 2H), 2.44 (s, 2H), 6.06 (s, 6H), 6.29 (s, 6H), 7.17–7.37 (m, 16H), 7.68 (m, 4H); IR ($CH_2Cl_2$) 2074, 2022, 1988, 1886, 1833 $cm^{-1}$; MS ($ESI^+$) *m/z* 832 $[M+Na]^+$ (5%), 453 (100%). Anal. Calc. for $C_{41}H_{36}N_3O_3P_3Mo$: C, 60.98; H, 4.49; N, 5.20. Found: C, 61.23; H, 4.50; N, 5.31%. For crystallographic data, see Table 1.

### 4.5. Preparation of $Mo(CO)_4$(bis(dipyrrolylphosphino)-binol)

A stirred solution of (*R*)-bis(dipyrrolylphosphino)-binol (0.647 g, 1.06 mmol) and molybdenum tetracarbonyl dipiperidine complex (0.420 g, 1.11 mmol) in 40 mL of toluene was heated at 100 °C for 3 h. After being allowed to cool to 20 °C, the reaction mixture was filtered through a pad of celite and the filtrate was concentrated under reduced pressure to give the crude product. Purification of this material was accomplished by flash chromatography on silica gel with 10% ethyl acetate in pentane to yield the title complex (0.650 g, 75%): mp 228–230 °C (dec); $^{31}P$ NMR (121.49 MHz, $CDCl_3$) $\delta$ 147.6 (s, 2P); $^1H$ NMR (300 MHz) $\delta$ 1.72 (s, 4H), 5.86 (s, 4H), 6.27 (d, $J$ = 9.0 Hz, 2H), 6.44 (s, 4H), 7.10 (s, 4H), 7.42 (d, $J$ = 3.8 Hz, 4H), 7.54 (br s, 2H), 7.88 (d, $J$ = 9.0 Hz, 2H), 7.95 (d, $J$ = 9.0 Hz, 2H); IR ($CH_2Cl_2$) 2082, 2048, 1948 $cm^{-1}$; MS ($ESI^+$) *m/z* 843 $[M + Na]^+$ (15%), 624 (17%), 453 (100%). Anal. Calc. for $C_{40}H_{28}N_4O_6P_2Mo$: C, 58.69; H, 3.45; N, 6.84. Found: C, 59.05; H, 3.50, N, 6.64%.

### 4.6. Preparation of mer-10

A stirred solution of freshly prepared $Mo(CO)_3(DMF)_3$ (0.600 g, 1.50 mmol) and bis(diphenylphosphino)ethane (0.598 g, 1.50 mmol) in 25 mL of dry toluene–DMF (4:1) was stirred at 20 °C for 3 h. Bis(dipyrrolylphosphino)-(*R*)-binol (0.916 g, 1.50 mmol) in 5 mL of toluene was then added and the reaction mixture was heated at 135 °C for 12 h. After being allowed to cool to 20 °C, the reaction

Table 1
Crystallographic data for *mer*-**9c** and *mer*-**10**

| | *mer*-**9c** | *mer*-**10** |
|---|---|---|
| Identification code | C2 | $P2_12_12_1$ |
| Crystal colour | Yellowish | Colourless |
| Crystal habit | Platelet | Block |
| Crystal size ($mm^3$) | $0.40 \times 0.40 \times 0.08$ | $0.40 \times 0.22 \times 0.10$ |
| Crystal behaviour under ambient conditions | Stable | Stable |
| Empirical formula | $(C_{53}H_{40}NMoO_5P_3)1{,}13(C_7H_8)$ | $C_{41}H_{36}N_3MoO_3P_3$ |
| $a$ (Å) | 21.575(4) | 11.638(2) |
| $b$ (Å) | 10.609(2) | 17.389(3) |
| $c$ (Å) | 24.918(5) | 18.716(2) |
| $\alpha$ (°) | 90 | 90 |
| $\beta$ (°) | 105.55(1) | 90 |
| $\gamma$ (°) | 90 | 90 |
| $V$ (Å$^3$) | 5495(2) | 3787.5(9) |
| $\lambda$ (Å) | 0.71073 | 0.71073 |
| Crystal system | Triclinic | Orthorhombic |
| Space group | $C2$ | $P2_12_12_1$ |
| $Z$ | 4 | 4 |
| Type of diffractometer | Bruker-Enraf-Nonius kappaCCD | Bruker-Enraf-Nonius kappaCCD |
| Method of data collection | $\phi$ and $\omega$ scans | $\phi$ and $\omega$ scans |
| Reflections collected | 33214 | 35710 |
| Independent reflections [$I > 2\sigma(I)$] | 4127 [$R_{(int)} = 0.0151$] | 10926 [R(int) = 0.0120] |
| Completeness of $\theta$ (°) | 1.00 (60) | 1.00 (54) |
| Absorption correction | None | None |
| $R$ [$I > 2\sigma(I)$] $w = 1/[\sigma^2(F_o)]$ | $R_1 = 0.0500$; $wR_2 = 0.0450$ | $R_1 = 0.0435$; $wR_2 = 0.0612$ |
| Number of parameters | 460 | 645 |
| Refinement method | Full-matrix least-squares on $F$ | Full-matrix least-squares on $F$ |
| Hydrogen atoms | Were set geometrically and recalculated before the last refinement cycle | Were set geometrically and recalculated before the last refinement cycle |

mixture was filtered through a pad of celite and the filtrate was concentrated under reduced pressure to give the crude product. Purification of this material was accomplished by flash chromatography on silica gel with 20% ethyl acetate in pentane to yield complex *mer*-**10** (0.848 g, 59%): mp 258–262 °C; $^{31}$P NMR (121.49 MHz, $CDCl_3$) $\delta$ 187.8 (dd, $^2J_{P-Pcis} = 28$ Hz, $^2J_{P-Ptrans} = 134$ Hz, 1P), 61.8 (d, $^2J_{P-Ptrans} = 140$ Hz, 1P), 54.4 (s, 1P); $^1$H NMR (300 MHz) $\delta$ 2.10–2.72 (m, 4H), 5.80 (s, 2H), 6.50–6.57 (m, 2H), 6.70 (m,2H), 6.87–7.95 (m, 30H); IR ($CH_2Cl_2$) 1992, 1962, 1937, 1882, 1836 $cm^{-1}$; HRMS $[M+Na]^+$: calc. for $C_{53}O_5P_3H_{40}NMoNa$: 984.10711; Found: 984.10631. For crystallographic data, see Table 1.

## Supplementary material

CCDC 675266, 675267 contain the supplementary crystallographic data for compounds *mer*-**9c** and *mer*-**10**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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