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Probing substituent effects in phosphinoamine ligands using $Mo(CO)_5L$ complexes

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ABSTRACT

Recent work has revealed substantial differences in the structure, spectroscopic properties, and reactivity of heterobimetallic Zr/Co complexes of the general form $XZr(R'NPR_2)_3CoY$ (R′ = ^{i}Pr, 2,4,6-trimethylphenyl, 3,5-dimethylphenyl; R = Ph, ^{i}Pr; X, Y = halides or neutral donor ligands) as a function of nitrogen and phosphorus donor atom substituents. To probe the electronic differences between these ligands, a series of $Mo(CO)_5(R_2PNHR')$ complexes has been synthesized (R = Ph, R′ = ^{i}Pr (**2a**); R = ^{i}Pr, R′ = ^{i}Pr (**2b**), 2,4,6-trimethylphenyl (**2c**), 3,5-dimethylphenyl (**2d**), 4-methylphenyl (**2e**), 4-trifluoromethylphenyl (**2f**), 4-methoxyphenyl (**2g**)). Thermolysis of $Mo(CO)_6$ with the corresponding phosphinoamine ligands **1a**–**1g** affords **2a**–**2g**. The infrared carbonyl stretching frequencies of these complexes have been compared to probe the effects of phosphorus and nitrogen substituents on the electronic properties of the phosphinoamine ligands.

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1. Introduction

In recent years, our group and others have been utilizing phosphinoamide ligands $[R'NPR_2]^-$ to link two metals in both homo- and hetero-bimetallic complexes [1–16]. These complexes have demonstrated remarkable reactivity, including CO_2 activation [17,18], E–H bond activation (E = S, O, N) [19,20], and catalytic activity towards hydrosilylation and cross-coupling reactions [21–23]. Varying the phosphine substituents in C_3-symmetric Zr/Co complexes $ClZr(^iPrNPR_2)_3CoI$ was shown to have a dramatic effect on the metal–metal interaction. The $^iPr_2P$-substituted complex has a Zr–Co distance 0.1 Å shorter than the Ph_2P-substituted complex, demonstrating that more electron-rich donor ligands increase the electron density at Co and allow for stronger Co → Zr dative donation [5]. More interestingly, however, the Zr-bound halide in the $^iPr_2P$-substituted complex $ClZr(^iPrNP^iPr_2)_3CoI$ becomes labile upon reduction, allowing the isolation of a coordinatively unsaturated complex $Zr(^iPrNP^iPr_2)_3CoN_2$ featuring a weakly-bound dinitrogen ligand on Co and an open coordination site at the trigonal pyramidal Zr center [24]. This, and another $^iPr_2P$-substituted complex $(THF)Zr(MesNP^iPr_2)_3CoN_2$ (Mes = (2,4,6-trimethylphenyl) [24] have demonstrated cooperative reactivity in which substrates add across the metal–metal bond, while the chloride-bound Ph_2P-substituted reduced product $[ClZr(^iPrNPPh_2)_3CoN_2]^-$ reacts in a manner similar to monometallic Co analogues, simply undergoing two-electron oxidation at the Co center [25].

Given the dramatic differences imparted by varying the phosphorus donor substituent, we have recently turned our attention to systematically investigating the implications of the amide donor substituents on metal–metal interactions and reactivity of heterobimetallic complexes. Comparison of the *N*-^{i}Pr and *N*-Mes derivatives $ClZr(RNP^iPr_2)_3CoI$ revealed identical Zr–Co distances, but redox potentials ca. 0.2 V more negative for the more electron-rich *N*-^{i}Pr derivative [5]. Structural and spectroscopic comparison of the reduced complexes $Zr(^iPrNP^iPr_2)_3CoN_2$ and $(THF)Zr(MesNP^iPr_2)_3CoN_2$ is complicated by the additional Zr-bound THF ligand on the *N*-Mes complex [24]. In a more subtle variation of the phosphinoamide N-donor substituent, we recently examined the *m*-xylyl derivative $[XylNP^iPr_2]^-$ (Xyl = 3,5,-dimethylphenyl) [23]. Interestingly, treatment of the metalloligand $(^iPr_2PNXyl)_3ZrCl$ with CoI_2 leads to the iodide-bridged product $(\eta^2\text{-}^iPr_2PNXyl)Zr(^iPr_2PNXyl)_2(\mu\text{-}I)CoI$ rather than the C_3-symmetric isomer observed for the *N*-Mes derivative $ClZr(MesNP^iPr_2)_3CoI$. Nonetheless, two electron-reduction of $(\eta^2\text{-}^iPr_2PNXyl)Zr(^iPr_2PNXyl)_2(\mu\text{-}I)CoI$ affords $(THF)Zr(XylNP^iPr_2)_3CoN_2$ for direct comparison with $(THF)Zr(MesNP^iPr_2)_3CoN_2$. Surprisingly, while the two complexes have similar Zr–Co distances, a remarkably large 20 cm^{-1} difference in $\nu(N_2)$ is observed by IR spectroscopy (2026 cm^{-1} versus 2045 cm^{-1}). Given the number of factors involved, this electronic difference can be attributed to two possibilities: (1) The amide substituents affect the electron density at the Zr center and this, in turn, strengthens

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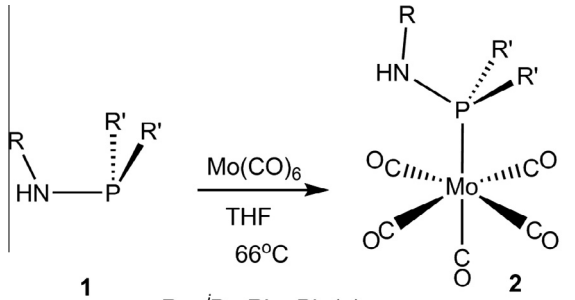
or weakens the metal–metal interaction. A less electron-rich Zr center could withdraw more electron density from Co via a stronger metal–metal interaction, leading to less back-bonding to N_2 and a higher $\nu(N_2)$. (2) The nitrogen substituents affect the donor ability of the phosphine, leading directly to a more or less electron-rich Co center. The nearly identical Zr–Co distances in (THF)Zr(XylNP^{i}Pr$_2$)$_3$CoN$_2$ and (THF)Zr(MesNP^{i}Pr$_2$)$_3$CoN$_2$ suggest that the latter hypothesis is more likely. In any case, the electronic differences between these two complexes have significant implications for reactivity and (THF)Zr(XylNP^{i}Pr$_2$)$_3$CoN$_2$ was shown to be a less effective catalysts for Kumada coupling reactions.

Herein, we use the Mo(CO)$_5$ fragment as a spectroscopic probe to investigate the variations in electron-donor ability of the phosphine moiety of a series of phosphinoamines in which the ligand substituents are systematically varied. Gray and coworkers previously investigated trends in ^{31}P and ^{95}Mo chemical shifts in a series of Mo(CO)$_5$(PPh$_2$XR) complexes (X = O, NH; R = alkyl, aryl) [26,27], but such a study with ^{i}Pr$_2$P-substituted phosphinoamines has not been reported. The implications of the electronic differences in a series of ^{i}Pr$_2$PNHR ligands are discussed in the context of heterobimetallic complexes.

2. Results and discussion

A series of Mo(CO)$_5$L complexes **2a**–**g** was synthesized via heating Mo(CO)$_6$ with R′NHPR$_2$ **1a**–**g** to 66 °C in THF in a sealed reaction vessel for 3 days (Scheme 1). The resulting products showed characteristic singlets in their ^{31}P NMR spectra shifted ~40–60 ppm downfield from the resonances observed for the phosphinoamine ligands (Table 1). Mono-substituted products were formed exclusively with the *N*-aryl-substituted ligands regardless of stoichiometry; however, small amounts of di-substituted Mo(CO)$_4$(L)$_2$ products were observed by ^{31}P NMR spectroscopy when *N*-^{i}Pr-substituted ligands were used. For example, heating a 1:1 mixture of Mo(CO)$_6$ and **1a** to 66 °C for 3 days typically leads to an 80:20 ratio of mono- and di-substituted products. The desired mono-substituted product **2a** can be separated from the mixture using column chromatography. In the case of **1b**, the mono-substituted product **2b**, could be obtained exclusively by using a slight excess (1.1 equiv) of Mo(CO)$_6$.

The solid state structures of two representative pentacarbonylmolybdenum complexes **2c** and **2e** were obtained using X-ray crystallography and are shown in Fig. 1. The Mo–C distances are in the 2.00–2.07 Å range, with the shortest Mo–C distances (Mo–C20 = 1.9973(15) Å (**2c**); Mo–C18 = 2.0092(11) Å (**2e**)) associated with the carbonyl groups *trans* to the phosphinoamine ligands. The Mo–P distances of **2c** and **2e** are 2.5616(4) Å, and 2.5492(3) Å, respectively. A structure for the Ph$_2$P-substituted analogue of **2e**, namely ((4-methylphenyl)NHP^{i}Pr$_2$)Mo(CO)$_5$, was previously reported and is largely similar to that of **2e** [30].



R = ^{i}Pr, R' = Ph (**a**)
R = R' = ^{i}Pr (**b**)
R = 2,4,6-trimethylphenyl, R' = ^{i}Pr (**c**)
R = 3,5-dimethylphenyl, R' = ^{i}Pr (**d**)
R = 4-methylphenyl, R' = ^{i}Pr (**e**)
R = 4-trifluoromethylphenyl, R' = ^{i}Pr (**f**)
R = 4-methoxyphenyl, R' = ^{i}Pr (**g**)

Scheme 1. Synthesis of complexes **2a**–**2g**.

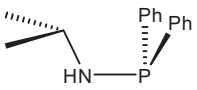
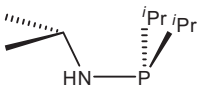
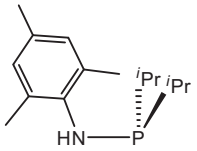
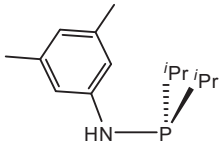
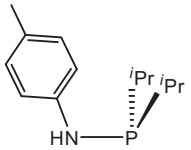
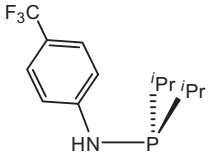
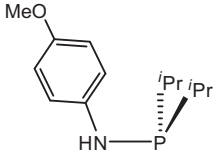
With a series of Mo(CO)$_5$(L) complexes in hand, infrared spectroscopy was used to probe the electron-donating ability of the phosphinamine ligands L. The spectra of all seven complexes feature three diagnostic carbonyl stretches, as is typical for pseudo C_{4v}-symmetric tricarbonyl compounds. On the basis of the evaluation of force constants, Cotton determined that the three stretches typically observed for Mo(CO)$_5$L complexes are most reasonably assigned as A_1, B_1, and overlapping A_1 and E vibrational modes [31]. The deviation from ideal C_{4v} symmetry imparted by the trisubstituted phosphine accounts for the observation of a B_1 mode, which would not be IR active in rigorous C_{4v} symmetry. In the series of Mo(CO)$_5$(Ph$_2$PNHR) complexes reported by Gray, there is no change in the carbonyl stretches as the R group is varied among different alkyl substituents (Me, Et, ^{i}Pr, ^{n}Bu, etc.) [26], and a very small (1–2 cm^{-1}) shift to higher frequency was observed upon changing the nitrogen substituents to aryl groups (Ph, *p*-tolyl) [27].

In the case of complexes **2a**–**2g**, a comparison of the highest frequency A_1 stretches reveals a variation of about 4 cm^{-1} across the series, with the highest ν(CO) for the Ph$_2$P-substituted phosphinoamine complex **2a** (Table 1).[1] While 4 cm^{-1} does not initially appear to be a large variation, the A_1 stretches of Mo(CO)$_5$(PR$_3$) complexes only vary within a ~10 cm^{-1} range. For example, the A_1 ν(CO) for Mo(CO)$_5$(PPh$_3$) is 2078 cm^{-1} while that for Mo(CO)$_5$(PMe$_3$) is 2071 cm^{-1} [32]. A comparison of the ν(CO) stretches of the two *N*-^{i}Pr complexes **2a** and **2b** reveals that variation of the phosphorus substituents from Ph to ^{i}Pr leads to a 4 cm^{-1} decrease in the frequency of the A_1 vibrational mode, as expected given the more electron-releasing nature of the alkyl substituents. Across the series of ^{i}Pr$_2$P-substituted complexes **2b**–**2g**, the CO stretches suggest that the ^{i}Pr$_2$PNHR ligands become more electron rich as the amine substituent is varied in the order 4-trifluoromethylphenyl < 4-methylphenyl = 3,5-dimethylphenyl < 4-methoxyphenyl < 2,4,6-trimethylphenyl = ^{i}Pr. Notably, the A_1 stretches of **2f** and **2a** are identical, suggesting that variation of the *N*-aryl substituents can affect electronic changes equivalent to varying the phosphine substituents. A careful examination of the chemical shifts and $^2J_{P-C}$ coupling constants associated with the metal carbonyls, particularly the CO ligand *trans* to the phosphinoamine phosphorus donor, in the ^{13}C NMR spectrum of **2a**–**2g** did not reveal any clear trends.

The trends in CO stretching frequencies of **2a**–**2g** and the corresponding trends in electron-donating ability of ligands **1a**–**1g** lends fundamental insight into some of the structural, spectroscopic, and reactivity trends observed in our group's heterobimetallic Zr/Co complexes. As suggested in the Introduction, the substantial differences in metal–metal interactions and reactivity of heterobimetallic Zr/Co complexes supported by deprotonated ligands **1a** and **1b**/**1c** can be attributed to the more electron-donating isopropyl phosphine substituents [5], and this is supported by the Mo(CO)$_5$L model studies. Based on the similar carbonyl stretching frequencies of **2b** and **2c**, the ~0.2 V difference in the redox potentials of ClZr(^{i}PrNP^{i}Pr$_2$)$_3$CoI and ClZr(MesNP^{i}Pr$_2$)$_3$CoI cannot be explained by electronic differences between the ligands and may more likely be the result of steric arguments – the larger mesityl substituent may better stabilize reduced products. Lastly, we find that the *N*-mesityl substituent does render ligand **1c** measurably more electron rich than *N*-xylyl ligand **1d**, a factor that likely plays a role in the substantial differences in the spectroscopic properties

[1] While all three infrared CO stretches generally follow the same trends, we discuss only the A1 mode here for simplicity.

Table 1
Infrared ν(CO) stretches of $Mo(CO)_5(L)$ complexes **2a–g**. ^{31}P NMR spectroscopic data for the $Mo(CO)_5(L)$ complexes and free ligands are also provided for comparison.

L =	ν(CO)[a] (cm^{-1})	$\delta^{31}P$ of **1**[b] (ppm)	$\delta^{31}P$ of **2**[b] (ppm)	$\delta^{13}C$ ($^2J_{P-C}$) for CO_{trans} and CO_{cis} in **2**[b]
	2071, 1988, 1937[d]	35.6 [28]	73.5[c]	211.1 (22.9 Hz) 206.1 (9.2 Hz)
1a 	2067, 1981, 1925	57.6 [5]	102.0	210.4 (22.9 Hz) 207.5 (9.3 Hz)
1b 	2067, 1982, 1935	57.7 [5]	105.8	210.2 (23.7 Hz) 207.1 (8.5 Hz)
1c 	2069, 1984, 1934	47.1 [23,29]	106.0	210.0 (23.7 Hz) 207.2 (9.3 Hz)
1d 	2069, 1983, 1932	48.7	106.1	210.0 (24.6 Hz) 207.2 (9.3 Hz)
1e 	2071, 1983, 1932	49.1	110.5	209.5 (24.4 Hz) 206.8 (9.1 Hz)
1f 	2068, 1983, 1935	51.0	110.5	210.2 (23.7 Hz) 207.3 (9.3 Hz)
1g				

[a] Spectra collected in C_6H_6 solution using a KBr solution cell.
[b] Spectra collected in C_6D_6.
[c] Previously reported ^{31}P NMR chemical shift of 74.18 ppm in $CDCl_3$ [26].
[d] Previously reported ν(CO) stretches of 2072, 1990, 1956, and 1947 in *n*-hexane using NaCl solution cell [26].

and reactivity of heterobimetallic Zr/Co complexes supported by these ligands [23]. The modulation of phosphine electronic properties by variation of *para*-phenyl substituents on the amine nitrogen is particularly remarkable given the distance of that substituent from the phosphorus donor atom.

3. Conclusions

In summary, we have synthesized a series of $Mo(CO)_5(R_2PNHR')$ complexes **2a–2g** and used infrared spectroscopy as a probe of the electronic properties of the phosphinoamine ligands as a function of nitrogen and phosphorus substituents. Variation of the phosphine substituents from aryl to alkyl leads to the expected decrease in ν(CO) as the phosphinoamines become more electron rich. A remarkably significant variation in the electronic properties of the phosphine donors was also observed upon varying the *N*-aryl substituents of the phosphinoamines. The ability to modulate ligand electronic properties via *N*-aryl substitution is in line with

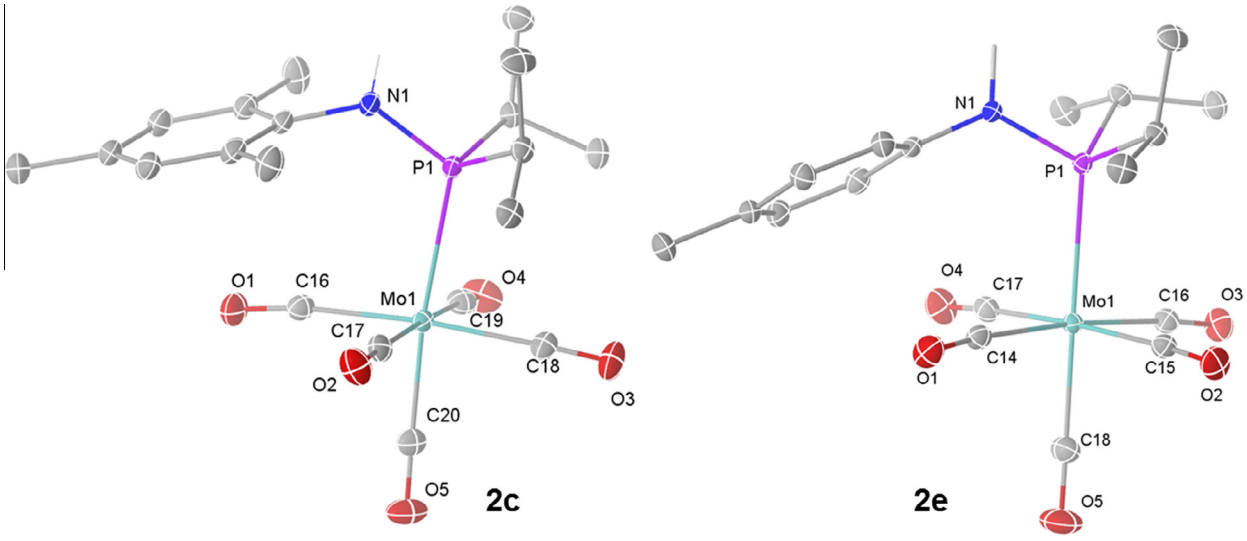


Fig. 1. Displacement ellipsoid (50%) representations of the solid state structures of **2c** and **2e**. Hydrogen atoms have been omitted for clarity. Relevant interatomic distances for **2c** (Å): Mo–P1, 2.5616(4); Mo–C16, 2.0528(14); Mo–C17, 2.0534(15); Mo–C18, 2.0468(14); Mo–C19, 2.0390(15); Mo–C20, 1.9973(15). Relevant interatomic distances for **2e** (Å): Mo–P1, 2.5492(3); Mo–C14, 2.0698(10); Mo–C15, 2.0539(10); Mo–C16, 2.0294(10); Mo–C17, 2.0377(10); Mo–C18, 2.0092(11).

the substantial differences we observe when these phosphinoamine ligands are deprotonated and used as a ligand platform to support C_3-symmetric heterobimetallic Zr/Co complexes. We do, however, expect that steric factors also play an important role and studies are currently underway to explore a series of heterobimetallic Zr/Co complexes in which the steric and electronic properties of the *N*-aryl substituents are systematically varied.

4. Experimental

4.1. General considerations

Unless specified otherwise, all manipulations were performed under an inert atmosphere using standard Schlenk or glovebox techniques. Glassware was oven dried before use. Tetrahydrofuran and pentane were purged with ultra high purity argon gas and dried using a Glass Contours solvent system with successive drying columns. All solvents were stored over 3 Å molecular sieves. Benzene-d_6 was degassed via repeated freeze–pump–thaw cycles and dried over 3 Å molecular sieves. ^{i}PrNHPPh$_2$ (**1a**) [28,33], ^{i}PrNHP^{i}Pr$_2$ (**1b**) [5], (2,4,6-trimethylphenyl)NHP^{i}Pr$_2$ (**1c**) [5], and (3,5-dimethylphenyl)NHP^{i}Pr$_2$ (**1d**) [23,29] were synthesized using literature procedures. All other chemicals were purchased from commercial vendors and used without further purification. All NMR spectra were recorded at ambient temperature unless otherwise noted and chemical shifts are reported in ppm. For ^{1}H and ^{13}C{^{1}H} NMR spectra, the solvent resonance was referenced as an internal standard, and for ^{31}P{^{1}H} NMR spectra the 85% H_3PO_4 resonance was referenced as an external standard (0 ppm). ^{19}F NMR spectra were referenced to 1% Trifloroacetic acid (−76.5 ppm). IR spectra were recorded on a Varian 640-IR spectrometer controlled by Resolutions Pro software. Elemental analyses were performed at Complete Analysis Laboratory Inc., Parsippany, NJ.

4.2. (4-methylphenyl)NHP^{i}Pr$_2$ (**1e**)

A solution of *p*-toluidine (5.00 g, 46.7 mmol) in toluene (60 mL) was cooled to −35 °C. To this was added a solution of sodium bis(trimethylsilyl)amide (8.56 g, 46.7 mmol) in toluene (40 mL) dropwise over five minutes. The resulting yellow solution was allowed to warm slowly to room temperature and stirred for four hours to ensure that a complete deprotonation had taken place. The resulting solution was cooled to −35 °C and a similarly cooled solution of chlorodiisopropylphosphine (7.4 mL, 47 mmol) in toluene (30 mL) was added dropwise. The reaction was warmed slowly to room temperature. After stirring for four hours, the reaction mixture was filtered through a pad of Celite, removing sodium chloride. The solvent was removed from the filtrate in vacuo. The resulting oily residue was redissolved in diethyl ether and filtered through a plug of silica gel. Removal of the solvent in vacuo yielded analytically pure product as a yellow oil (9.2 g, 88%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.03 (d, 2H, ^{2}J = 8.4 Hz, Ar-H), 6.96 (m, 2H, J = 8.0 Hz, Ar-H), 3.74 (d, 1H, $^{2}J_{H-P}$ = 10.8 Hz, NH), 2.31 (s, 3H, Me), 1.82 (m, 2H, C*H*(CH$_3$)$_2$), 1.15 (m, 12H, CH-(C*H*$_3$)$_2$). ^{31}P{^{1}H} NMR (161.8 MHz, C_6D_6): δ = 48.9 (s). ^{13}C NMR (100.5 MHz, CD_2Cl_2): δ = 147.3 (d, J = 16.1 Hz, N-*ipso*-Ar), 130.1 (s, Ar), 127.9 (s, *ipso*-Ar), 116.4 (d, J = 12.3 Hz, Ar), 27.4 (d, J = 12.1 Hz, *C*H(CH$_3$)$_2$), 20.8 (s, tolyl-Me) 19.3 (d, J = 20.3 Hz, CH(C*H*$_3$)$_2$) 17.5 (d, J = 8.1 Hz, CH(C*H*$_3$)$_2$). *Anal.* Calc. for $C_{13}H_{19}F_3NP$: C, 69.93; H, 9.93; N, 6.27. Found: C, 69.79; H, 9.87; N, 6.30%.

4.3. (4-trifluoromethylphenyl)NHP^{i}Pr$_2$ (**1f**)

A solution of 4-(trifluoromethyl)aniline (5.00 g, 31.0 mmol) in toluene (60 mL) was cooled to −35 °C. To this was added a solution of sodium bis(trimethylsilyl)amide (6.25 g, 34.1 mmol) in toluene (40 mL) dropwise over five minutes. The resulting yellow solution was allowed to warm slowly to room temperature. The reaction was stirred at room temperature for four hours to ensure that deprotonation had proceeded completely. The resulting solution was cooled to −35 °C and to this a similarly cooled solution of chlorodiisopropylphosphine (4.93 mL, 31.0 mmol) in toluene (30 mL) was added dropwise. The reaction was warmed slowly to room temperature. After stirring for four hours at room temperature, the reaction mixture was filtered through a pad of Celite, removing sodium chloride. The solvent was removed from the filtrate in vacuo and the resulting oily residue was redissolved in diethyl ether and filtered through a plug of silica gel. Removal of the solvent from the filtrate in vacuo yielded analytically pure product as a yellow oil (7.90 g, 91.7%). ^{1}H NMR (400 MHz, C_6D_6): δ 7.32 (d, J = 7.6 Hz, 2H, Ar), 6.78 (d, J = 7.6 Hz, 2H, Ar), 3.56 (d, J = 6.8 Hz, 1H, NH), 1.39 (m, 2H, C*H*(CH$_3$)$_2$), 0.87 (m, 12H,

$CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (100.5 MHz, CD_2Cl_2): δ 153.0 (d, J = 16.3 Hz, N-*ipso*-Ar), 126.3 (m, Ar), 119.5 (q, $^2J_{C-F}$ = 33.3 Hz, ipso-CF_3), 125.2 (q, $^1J_{C-F}$ = 270.4 Hz, CF_3), 115.3 (d, J = 13.0 Hz, Ar), 26.6 (d, J = 11.4 Hz, $CH(CH_3)_2$), 18.5 (d, J = 20.3 Hz, $CH(CH_3)_2$), 16.8 (d, J = 7.3 Hz, $CH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (161.8 MHz, C_6D_6): δ 49.1 (s). ^{19}F NMR (376.1 MHz, C_6D_6): δ 14.96 (s). *Anal.* Calc. for $C_{13}H_{19}F_3NP$: C, 56.31; H, 6.91; N, 5.05. Found: C, 56.36; H, 6.89; N, 5.09%.

4.4. (4-methoxyphenyl)NHP^{i}Pr$_2$ (**1g**)

A solution of p-anisidine (5.00 g, 40.6 mmol) in toluene (60 mL) was cooled to −35 °C. To this was added a solution of sodium bis(trimethylsilyl)amide (7.44 g, 40.6 mmol) in toluene (40 mL) dropwise over five minutes. The resulting yellow solution was allowed to warm slowly to room temperature. The reaction was stirred at room temperature for four hours to ensure that a complete deprotonation had taken place. The resulting solution was cooled to −35 °C and to this a cold solution of chlorodiisopropylphosphine (6.46 mL, 40.6 mmol) in toluene (30 mL) was added dropwise. The reaction was warmed slowly to room temperature. After stirring for four hours, the reaction mixture was filtered through a pad of Celite, removing sodium chloride. The solvent was removed from the filtrate in vacuo. The resulting oily residue was redissolved in diethyl ether and filtered through a plug of silica gel. Removal of the solvent from the filtrate in vacuo yielded analytically pure product as a yellow oil (8.73 g, 89.9%). ^1H NMR (400 MHz, C_6D_6): δ 6.93 (d, J = 8.8 Hz, 2H, Ar), 6.78 (d, J = 10.4 Hz, 2H, Ar), 3.37 (s, 3H, MeO), 3.14 (d, J = 10.4 Hz, 1H, NH), 1.46 (m, 2H, $CH(CH_3)_2$), 0.96 (m, 12H, $CH(CH_3)_2$). $^{31}P\{_1H\}$ NMR (161.8 MHz, C_6D_6): δ 51.0 (s). $^{13}C\{^1H\}$ NMR (100.5 MHz, CD_2Cl_2): δ 152.6 (s, *ipso*-OMe), 142.9 (d, J = 16.3 Hz, N-*ipso*-Ar), 116.8 (d, J = 10.6 Hz, Ar), 114.5 (s, Ar), 55.52 (s, OMe), 26.85 (d, J = 11.4 Hz, $CH(CH_3)_2$), 18.8 (d, J = 20.3 Hz, $CH(CH_3)_2$), 17.0 (d, J = 8.0 Hz, $CH(CH_3)_2$). *Anal.* Calc. for $C_{13}H_{19}F_3NP$: C, 65.25; H, 9.27; N, 5.85. Found: C, 65.28; H, 9.36; N, 5.84%.

4.5. (^{i}PrNHPPh$_2$)Mo(CO)$_5$ (**2a**)

Solid $Mo(CO)_6$ (264.0 mg, 1.000 mmol) and ^{i}PrNHPPh$_2$ (243.4 mg, 1.000 mmol) were combined in THF (10 mL) in a pressure flask under N_2. The flask was sealed tightly and heated to 66 °C for 3 days. The reaction vessel was then brought into a glovebox and the reaction mixture was filtered to remove insoluble impurities. The filtrate was then dried under vacuum. The remaining solids were washed with cold pentane (2 mL) and the product was dried in vacuo, leaving an off-white solid. Isolated product typically contains a small amount (20% or less) of disubstituted product, (^{i}PrNHPPh$_2$)$_2$Mo(CO)$_4$, which can be separated using column chromatography (5:1 CH_2Cl_2/hexanes) (yield: 291.5 mg, 61%). ^1H NMR (400 MHz, C_6D_6): δ 7.52 (m, 4H, Ph), 7.05 (m, 6H, Ph), 2.90 (m, 1H, $CH(CH_3)_2$), 1.73 (m, 1H, NH), 0.55 (d, J = 6.0 Hz, 6H). $^{13}C\{^1H\}$ NMR (100.5 MHz, C_6D_6): δ 211.1 (d, J = 22.9 Hz, Mo–CO), 206.1 (d, J = 9.2 Hz, Mo–CO), 139.1 (d, J = 40.7 Hz, P-*ipso*-Ph), 131.9 (d, J = 13.5 Hz, Ph), 130.5 (s, Ph), 129.0 (d, J = 9.3 Hz, Ph), 47.2 (d, J = 5.9 Hz, $CH(CH_3)_2$), 25.6 (d, J = 3.3 Hz, $CH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (161.8 MHz, C_6D_6): δ 73.5. FT-IR(C_6D_6, KBr): 2071 cm^{-1}, 1988 cm^{-1}, 1937 cm^{-1}. *Anal.* Calc. for $C_{20}H_{19}MoNO_5P$: C, 50.01; H, 3.99; N, 2.92. Found: C, 50.08; H, 3.91; N, 3.01%. Spectroscopic properties are consistent with those previously reported for **2a** synthesized via a different route.[26].

4.6. (^{i}PrNHP^{i}Pr$_2$)Mo(CO)$_5$ (**2b**)

Solid $Mo(CO)_6$ (290.4 mg, 1.100 mmol) and ^{i}PrNHP^{i}Pr$_2$ (175.3 mg, 1.000 mmol) were combined in THF (10 mL) in a pressure flask under N_2. The flask was sealed tightly and heated to 66 °C for 3 days. The reaction vessel was then brought into a glovebox and the reaction mixture was filtered to remove insoluble impurities. The filtrate was then dried under vacuum. The remaining solids were washed with cold pentane (2 mL) and the product was dried in vacuo, leaving a yellow solid (324.2 mg, 78%). Note: Small amounts of disubstituted product, (^{i}PrNHP^{i}Pr$_2$)$_2$Mo(CO)$_4$, were formed when stoichiometry was not carefully controlled. ^1H NMR (400 MHz, C_6D_6): δ 3.04 (m, 1H, $NCH(CH_3)_2$), 1.51 (m, 2H, $PCH(CH_3)_2$), 0.96 (m, 6H, $PCH(CH_3)_2$), 0.85 (m, 6H, $PCH(CH_3)_2$), 0.85 (d, 6H, $NCH(CH_3)_2$), 0.61 (m, 1H, NH). $^{13}C\{^1H\}$ NMR (100.5 MHz, C_6D_6): δ 210.4 (d, J = 22.9 Hz, Mo–CO), 207.5 (d, J = 9.3 Hz, Mo–CO), 47.4 (s, $NCH(CH_3)_2$), 30.1 (d, J = 22.8, $PCH(CH_3)_2$), 26.9 (d, J = 2.6 Hz, $NCH(CH_3)_2$), 18.1 (d, J = 6.7 Hz, $PCH(CH_3)_2$), 17.5 (s, $PCH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (161.8 MHz, C_6D_6): δ 102.0. FT-IR (C_6H_6, KBr): 2067 cm^{-1}, 1981 cm^{-1}, 1925 cm^{-1}. *Anal.* Calc. for $C_{14}H_{22}MoNO_5P$: C, 40.89; H, 5.39; N, 3.41. Found: C, 41.11; H, 5.44; N, 2.91%.

4.7. ((2,4,6-trimethylphenyl)NHP^{i}Pr$_2$)Mo(CO)$_5$ (**2c**)

Solid $Mo(CO)_6$ (264.0 mg, 1.000 mmol) and (2,4,6-trimethylphenyl)NHP^{i}Pr$_2$ (251.4 mg, 1.000 mmol) were combined in THF (10 mL) in a pressure flask under N_2. The flask was sealed tightly and heated to 66 °C for 3 days. The reaction vessel was then brought into the glovebox and the reaction mixture was filtered to remove insoluble impurities. The filtrate was then dried under vacuum. The remaining solids were washed with cold pentane (2 mL) and the product was dried in vacuo, leaving an off-white solid (374.3 mg, 77%). ^1H NMR (400 MHz, C_6D_6): δ 6.69 (s, 2H, Mes-Ar), 2.58 (s, 1H, NH), 2.11 (s, 6H, Mes-CH_3), 2.04 (m, 2H, $CH(CH_3)_2$), 0.92–1.04 (m, 12H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (100.5 MHz, C_6D_6): δ 210.2 (d, J = 23.7 Hz, Mo–CO), 207.1 (d, J = 8.5 Hz, Mo–CO), 138.7 (d, J = 2.6 Hz, Mes-Ar), 136.4 (d, J = 2.5 Hz, Mes-Ar), 135.9 (d, J = 1.7 Hz), 130.4 (s, Mes-Ar), 32.3 (d, J = 18.7 Hz, $CH(CH_3)_2$), 21.1 (s, Mes-Me), 20.9 (s, Mes-Me), 19.3 (m, $CH(CH_3)_2$, 2 peaks overlapping). $^{31}P\{^1H\}$ NMR (161.8 MHz, C_6D_6): δ 105.8. FT-IR(C_6D_6): 2067 cm^{-1}, 1982 cm^{-1}, 1935 cm^{-1}. *Anal.* Calc. for $C_{20}H_{26}MoNO_5P$: C, 49.29; H, 5.38; N, 2.87. Found: C, 49.40; H, 5.42; N, 3.02%.

4.8. ((3,5-dimethylphenyl)NHP^{i}Pr$_2$)Mo(CO)$_5$ (**2d**)

Solid $Mo(CO)_6$ (152.0 mg, 0.578 mmol) and (3,5-dimethylphenyl)NHP^{i}Pr$_2$ (137.4 mg, 0.578 mmol) were combined with THF (10 mL) in a pressure flask under N_2. The flask was sealed tightly and heated to 66 °C for 3 days. The reaction was then brought into a glovebox and the reaction mixture was filtered to remove insoluble impurities. The filtrate was then dried under vacuum. The remaining solids were washed with cold pentane (2 mL) and the product was dried in vacuo, leaving an off-white solid product (180.8 mg, 66%). ^1H NMR (400 MHz, C_6D_6): δ 6.52 (s, 1H, Ar), 6.44 (s, 2H, Ar), 3.51 (d, 1H, J = 8.0 Hz, NH), 2.11(s, 6H, ArMe), 2.00 (m, 2H, $CH(CH_3)_2$), 0.92–1.03 (m, 12H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (100.5 MHz, C_6D_6): δ 210.0 (d, J = 23.7 Hz, Mo–CO), 207.2 (d, J = 9.3 Hz, Mo–CO), 143.9 (d, J = 5.1 Hz, N-*ipso*-Ar), 139.3 (s, Ar), 125.2 (s, Ar), 120.3 (s, Ar), 31.1 (d, J = 20.3 Hz, $CH(CH_3)_2$), 21.6 (s, Ar-Me), 18.8 (d, J = 8.5 Hz, $CH(CH_3)_2$), 18.1 (s, $CH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (161.8 MHz, C_6D_6): δ 106.0. FT-IR (C_6D_6, KBr): 2069 cm^{-1}, 1984 cm^{-1}, 1934 cm^{-1}. *Anal.* Calc. for $C_{19}H_{24}MoNO_5P$: C, 48.21; H, 5.11; N, 2.96. Found: C, 48.17; H, 5.08; N, 3.05%.

4.9. ((4-methylphenyl)NHP^{i}Pr$_2$)Mo(CO)$_5$ (**2e**)

Solid $Mo(CO)_6$ (264.0 mg, 1.000 mmol) and (4-methylphenyl)NHP^{i}Pr$_2$ (223.3 mg, 1.087 mmol) were combined with

THF (10 mL) in a pressure flask under N_2. The flask was sealed tightly and heated to 66 °C for 3 days. The reaction vessel was then brought into a glovebox and the reaction mixture was filtered to remove insoluble impurities. The filtrate was then dried under vacuum. The remaining solids were washed with cold pentane (2 mL) and the product was dried in vacuo, leaving an off-white solid product (316.9 mg, 69%). ^{1}H NMR (400 MHz, C_6D_6): δ 6.87 (d, J = 7.2 Hz, 2H, Ar), 6.59 (d, J = 8.0 Hz, 2H, Ar), 3.52 (d, J = 10 Hz, 1H, NH), 2.10 (s, 3H, Ar-Me), 1.97 (m, 2H, C*H*(CH_3)$_2$), 0.85–1.02 (m, 12H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6): δ 210.0 (d, J = 24.6 Hz, Mo–CO), 207.2 (d, J = 9.3 Hz, Mo–CO), 141.3 (d, J = 6.8 Hz, N-*ipso*-Ar), 132.8 (s, *ipso*-Ar), 130.3 (s, Ar), 122.8 (d, J = 3.4 Hz, Ar), 30.9 (d, J = 21.2 Hz, *C*H(CH_3)$_2$), 21.0 (s, *p*-*C*H$_3$), 18.8 (d, J = 8.4 Hz, CH(*C*H$_3$)$_2$), 18.1 (s, CH(CH_3)$_2$). ^{31}P{^{1}H} NMR (161.8 MHz, C_6D_6): δ 106.1. FT-IR (C_6H_6, KBr): 2069 cm^{-1}, 1983 cm^{-1}, 1932 cm^{-1} *Anal.* Calc. for $C_{18}H_{22}MoNO_5P$: C, 47.07; H, 4.83; N, 3.05. Found: C, 46.96; H, 4.79; N, 3.10%.

4.10. ((4-trifluoromethylphenyl)NHP^{i}Pr$_2$)Mo(CO)$_5$ (**2f**)

Solid $Mo(CO)_6$ (264.0 mg, 1.000 mmol) and (*p*-CF_3-C_6H_4)NHP^{i}Pr$_2$ (277.1 mg, 1.000 mmol) were combined with THF (10 mL) in a pressure flask under N_2. The flask was sealed tightly and heated to 66 °C for 3 days. The reaction vessel was then brought into a glovebox and the reaction mixture was filtered to remove insoluble impurities. The filtrate was then dried under vacuum. The remaining residue was washed with cold pentane (2 mL) and the product was dried in vacuo, leaving a yellow oily product (356.0 mg, 66%). ^{1}H NMR (400 MHz, C_6D_6): δ 7.25 (d, J = 8.4 Hz, 2H, Ar), 6.34 (d, J = 8.4 Hz, 2H, Ar), 3.80 (d, J = 10.4 Hz, 1H, NH), 1.91 (m, 2H, C*H*(CH_3)$_2$), 0.79–0.94 (m, 12H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6): δ 209.5 (d, J = 24.4 Hz, Mo–CO), 206.8 (d, J = 9.1 Hz, Mo–CO), 147.2 (d, J = 7.6 Hz, N-*ipso*-Ar), 127.1 (q, J = 3.8 Hz, Ar), 125.5 (q, $^1J_{C-F}$ = 270.7 Hz, *C*F$_3$), 124.2 (q, $^2J_{C-F}$ = 32.0 Hz, *ipso*-CF_3), 120.0 (d, J = 3.0 Hz, Ar), 30.8 (d, J = 19.1 Hz, *C*H(CH_3)$_2$), 19.0 (d, J = 9.1 Hz, CH(*C*H$_3$)$_2$), 18.2 (s, CH(*C*H$_3$)$_2$). ^{19}F NMR (376.1 MHz, C_6D_6): δ -65.9. ^{31}P{^{1}H} NMR (161.8 MHz, C_6D_6): δ 110.5. FT-IR(C_6H_6, KBr): 2071 cm^{-1}, 1983 cm^{-1}, 1932 cm^{-1}. *Anal.* Calc. for $C_{18}H_{19}F_3MoNO_5P$: C, 42.12; H, 3.73; N, 2.73. Found: C, 42.25; H, 3.77; N, 2.96%.

4.11. ((4-methoxyphenyl)NHP^{i}Pr$_2$)Mo(CO)$_5$ (**2g**)

Solid $Mo(CO)_6$ (264.0 mg, 1.000 mmol) and (*p*-OMe-C_6H_4)-NHP^{i}Pr$_2$ (223.3 mg, 0.934 mmol) were combined with THF (10 mL) in a pressure flask under N_2. The flask was sealed tightly and heated to 66 °C for 3 days. The reaction vessel was then brought into a glovebox and the reaction mixtures was filtered to remove insoluble impurities. The filtrate was then dried under vacuum. The remaining solids were washed with cold pentane (2 mL) and the product was dried in vacuo, leaving an off-white solid (396.5 mg, 86.3%). ^{1}H NMR (400 MHz, C_6D_6): δ 6.67 (br, 4H, overlapping Ar), 3.46 (d, J = 8.8 Hz, 1H, NH), 3.33 (s, 3H, OMe), 1.88 (m, 2H, C*H*(CH_3)$_2$), 0.91–1.06 (m, 12H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6): δ 210.2 (d, J = 23.7 Hz, Mo–CO), 207.3 (d, J = 9.3 Hz), 157.1 (s, *ipso*-OMe), 136.5 (d, J = 5.9 Hz, N-*ipso*-Ar), 126.0 (d, J = 2.6 Hz, Ar), 114.9 (s, Ar), 55.4 (s, O*C*H$_3$), 30.8 (d, J = 21.2 Hz, *C*H(CH_3)$_2$), 18.6 (d, J = 7.6 Hz, CH(CH_3)$_2$), 17.9 (s, CH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (161.8 MHz, C_6D_6): δ 110.5. FT-IR (C_6H_6, KBr): 2068 cm^{-1}, 1983 cm^{-1} 1935 cm^{-1} *Anal.* Calc. for $C_{18}H_{22}$-$MoNO_6P$: C, 45.49; H, 4.67; N, 2.95. Found: C, 45.62; H, 4.71; N, 3.09%.

4.12. X-ray crystallography procedures

All operations were performed on a Bruker–Nonius Kappa Apex2 diffractometer, using graphite monochromated Mo Kα radiation. All diffractometer manipulations, including data collection, integration, scaling, and absorption corrections were carried out using the Bruker Apex2 software [34]. Preliminary cell constants were obtained from three sets of 12 frames. All crystal structure refinements were performed on F^2. Data collection and refinement parameters are presented in Table 2, and fully labelled diagrams and data collection and refinement details are included in the Supplementary Information File.

Table 2
X-ray diffraction data collection and refinement details for **2c** and **2e**.

	2c	**2e**
Chemical formula	$C_{20}H_{26}MoNO_5P$	$C_{18}H_{22}MoNO_5P$
Formula Weight	487.34	459.29
T (K)	120	120
λ (Å)	0.71073	0.71073
a (Å)	8.6036(4)	8.9673(8)
b (Å)	9.552(4)	9.4854(8)
c (Å)	13.7106(6)	13.1572(12)
α (°)	94.4000(19)	98.406(3)
β (°)	93.502(2)	95.418(4)
γ (°)	105.3196(19)	111.829(3)
V (Å^3)	1079.66(5)	1014.15(16)
Space group	$P\bar{1}$	$P\bar{1}$
Z, Z'	2, 1	2, 1
D_{calc} (g cm^{-3})	1.499	1.504
μ (cm^{-1})	0.711	0.752
R_1[a] ($I > 2\sigma$)	0.0213	0.0162
wR_2[a] (all data)	0.0541	0.0429

[a] $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$, $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

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Appendix A. Supplementary data

CCDC 1023206–1023207 contain the supplementary crystallographic data for **2c** and **2e**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2014.12.005.

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