

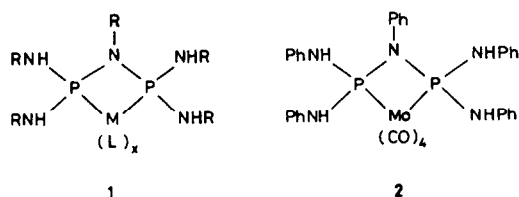
Synthesis and Characterization of a Primary Amine-Substituted Bis(phosphino)amine Metal Complex *cis*-PhN[P(NHPh)₂]₂Mo(CO)₄

HAW-JAN CHEN, ABBAS TARASSOLI, R. CURTIS HALTIWANGER, VILOYA S. ALLURED and ARLAN D. NORMAN

Department of Chemistry, University of Colorado, Boulder, Co. 80309, U.S.A.

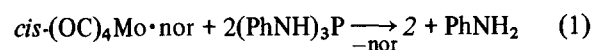
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Primary amine-substituted bis(phosphino)amine–metal complexes (1), because of their NH bond functionality are potentially valuable intermediates for

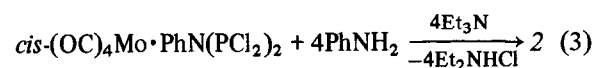
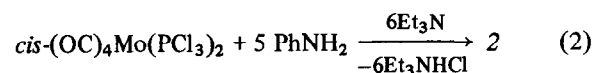


the synthesis of variously substituted, bis(phosphino)amine–metal complexes. However, because primary amine substituted bis(phosphino)amines are generally unstable and therefore difficult to isolate, [1, 2], their direct reaction with metals to form complexes has been unexplored. We now wish to report the preparation and characterization of a bis(phosphino)amine–molybdenum complex (2), in reactions which take advantage of metal coordination to stabilize key intermediate species. The reactions not only provide a route to novel compounds, but they are also examples of P–N–P skeleton formation reactions which take advantage of a metal template.

Compound 2 was formed by three methods according to the reactions given in equations 1–3.



nor = norbornadiene



Cis-(OC)₄Mo·nor [3], *cis*-(OC)₄Mo(PhNH)₂ [4], and *cis*-(OC)₄Mo·PhN(Ph)₂ [5] react smoothly with (C₆H₅NH)₃P or C₆H₅NH₂ in toluene under N₂ at 0 °C as shown. From the reaction in equation 1, 2

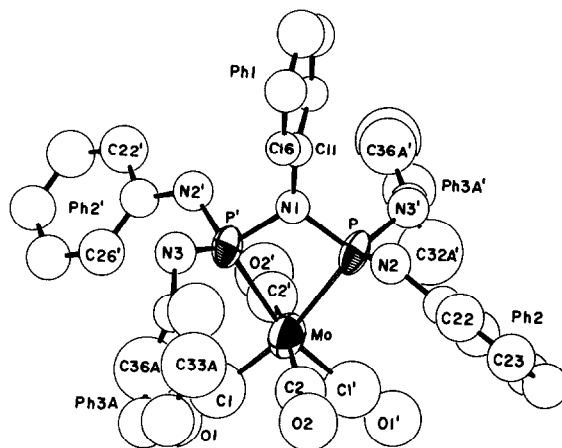


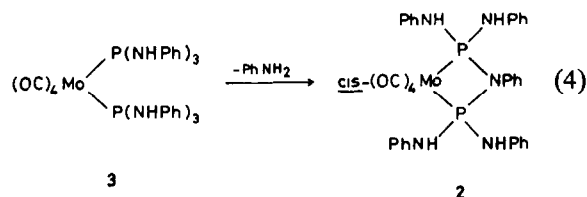
Fig. 1. The molecular structure of *cis*-(OC)₄Mo[P(NHPh)₂]₂-NPh. Hydrogen atoms are omitted for clarity and only one of two positions of disorder for Ph3, A, is shown. Primed atoms are related to unprimed atoms by the appropriate symmetry operations. Selected bond distances (Å) are: Mo–P, 2.48(1); P–N(1), 1.71(2); P–N(2), 1.65(2); P–N(3), 1.66(3); Mo–Cl, 1.94(5) and Cl–O(1), 1.15(4). Selected bond angles (deg) are: P–Mo–P', 65.8(4); Mo–P–N(1), 95.2(7); P–N(1)–P', 104(2); Mo–P–N(2), 123(1); Mo–P–N(3), 126(1); N(2)–P–N(3), 100(1); N(1)–P–N(3), 110(1); and N(1)–P–N(2), 99(1).

is isolated by its crystallization from the reaction mixture after removal *in vacuo* of most solvent and PhNH₂. From reactions 2 and 3, 2 is crystallized from the reaction mixture after removal of Et₃NHCl by filtration and removal of some solvent and excess Et₃N *in vacuo*. Yields of 2 from reactions in equations 1, 2, and 3, are typically 50%, 60%, and 80%, respectively. Recrystallization from benzene or toluene yields pure crystalline 2·½(C₆H₅) or 2·½(C₇H₈) [6]. *Spectral Data for 2*: Mass; parent ion at *m/e* 731; IR (mineral oil), characteristic absorptions at 3402 and 3380 (NH) and 2024, 1924, 1912, 1888, and 1878 (CO) cm⁻¹; ³¹P NMR (C₆D₆), δ 96.0 ppm; ¹H NMR (CD₂Cl₂), δ 4.95 ppm (NH, area 4) and δ 6.78–7.56 ppm (C₆H₅, area 25).

Unambiguous structural characterization of 2·½(C₆H₆) is based on a single crystal X-ray study [7]. The structure solution was based on 539 observed independent reflections. The molybdenum atoms were located by direct methods and other non-hydrogen atoms by three dimensional difference maps. Refinement of the structure, treating phenyl groups as rigid groups and molybdenum, phosphorous and nitrogen atoms anisotropically, was accomplished to R = 0.078 and wR = 0.089. The benzene solvent is present in a ratio of one-half molecule per molecule of 2. The structure of 2, Fig.1, consists of a planar ring of two phosphorus, one nitrogen, and one molybdenum atom. Several bond distances and angles

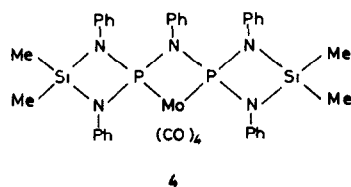
in the $\text{PhN}[\text{P}(\text{NHPh})_2]_2$ unit [2] are affected slightly by coordination to the $\text{Mo}(\text{CO})_4$ moiety. The P–N1 distance increases from 1.69(1) Å (mean) to 1.71(2) Å, the mean P–N (exo) distance decreases from 1.69(1) Å to 1.66(2) Å, and the P–N–P angle decreases from 118 to 104° upon coordination. Attempts to rationalize these effects are part of a theoretical study of bonding in P–N compounds currently in progress in our laboratories.

^{31}P NMR analysis of the $\text{cis}-(\text{OC})_4\text{Mo}\cdot\text{nor}-(\text{PhNH})_3\text{P}[\text{P}(\text{NHPh})_2]_2$ reaction mixture shows that formation of 2 is preceded by formation of a species (3) which yields a singlet spectral resonance at δ 108.4 ppm. Similarly, 3 forms prior to 2 in the $\text{cis}-(\text{OC})_4\text{Mo}-(\text{PCl}_3)_2-\text{PhNH}_2$ reaction. Because 3, upon removal of PhNH_2 undergoes conversion to 2, 3 is characterized tentatively as $\text{cis}-(\text{OC})_4\text{Mo}[\text{P}(\text{NHPh})_3]_2$. Our data indicate that 3 upon PhNH_2 loss, undergoes P–N bond condensation (equation 4) in an interesting example of a metal-templated P–N bond condensation process. Reactions of this type, *i.e.* reactions of primary amines with $\text{cis}-(\text{OC})_4\text{Mo}(\text{PCl}_3)_2$ or primary



aminophosphines with $\text{cis}-(\text{OC})_4\text{Mo}$ nor could have general synthetic utility. However, since primary aminophosphines are generally unstable and difficult to isolate, reactions of the type shown in equation 2 may have greater potential. In those cases where the $\text{Rn}(\text{PCl}_2)_2$ species can be prepared and coordinated to a metal moiety, syntheses of primary amine-substituted bis(phosphino)amine–metal complexes by reactions of the type shown in equation 3 appear quite viable also.

Preliminary experiments indicate 2 is a species upon which novel derivatization can be based. Reaction of 2 with Me_2SiCl_2 in the presence of excess Et_3N yields a product characterized tentatively as 4. In contrast, reaction of Me_2SiCl_2 with uncoordinated $\text{PhN}[\text{P}(\text{NHPh})_2]_2$ in the presence of excess Et_3N appears to yield only intractable products.



Acknowledgements

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- 6 Satisfactory elemental analytical data for $2 \cdot \frac{1}{2}(\text{C}_7\text{H}_8)$ were obtained.
- 7 The crystals of $2 \cdot \frac{1}{2}(\text{C}_6\text{H}_6)$ are hexagonal, space group P6_122 , with 6 molecules in a unit cell of dimensions $a = 15.606(4)$, $b = 15.606(4)$, and $c = 28.721(4)$ Å.