Inorganica Chimica Acta, 65 (1982) L69–L70

Synthesis and Characterization of a Primary Amine-Substituted Bis(phosphino)amine Metal Complex *cis*-PhN[P(NHPh)$_2$]$_2$Mo(CO)$_4$

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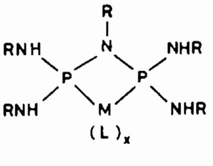
Received February 25, 1982

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.



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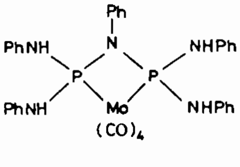

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Compound *2* was formed by three methods according to the reactions given in equations 1–3.

$$cis\text{-}(OC)_4Mo\cdot nor + 2(PhNH)_3P \xrightarrow[-nor]{} 2 + PhNH_2 \qquad (1)$$

nor = norbornadiene

$$cis\text{-}(OC)_4Mo(PCl_3)_2 + 5\ PhNH_2 \xrightarrow[-6Et_3NHCl]{6Et_3N} 2 \qquad (2)$$

$$cis\text{-}(OC)_4Mo\cdot PhN(PCl_2)_2 + 4PhNH_2 \xrightarrow[-4Et_2NHCl]{4Et_3N} 2 \qquad (3)$$

Cis-(OC)$_4$Mo·nor [3], *cis*-(OC)$_4$Mo(PCl$_3$)$_2$ [4], and *cis*-(OC)$_4$Mo·PhN(PCl$_2$)$_2$ [5] react smoothly with (C$_6$H$_5$NH)$_3$P or C$_6$H$_5$NH$_2$ in toluene under N$_2$ at 0 °C as shown. From the reaction in equation 1, *2* is isolated by its crystallization from the reaction mixture after removal *in vacuo* of most solvent and PhNH$_2$. From reactions 2 and 3, *2* is crystallized from the reaction mixture after removal of Et$_3$NHCl by filtration and removal of some solvent and excess Et$_3$N *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(C$_6$H$_5$) or *2*·½(C$_7$H$_8$) [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}; ^{31}P NMR (C$_6$D$_6$), δ 96.0 ppm; ^{1}H NMR (CD$_2$Cl$_2$), δ 4.95 ppm (NH, area 4) and δ 6.78–7.56 ppm (C$_6$H$_5$, area 25).

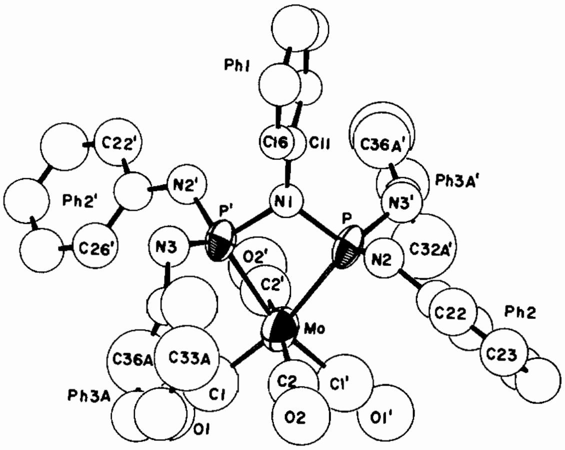


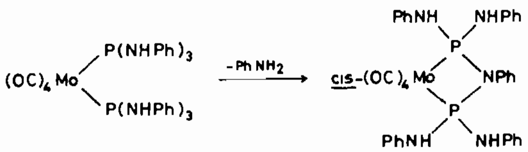
Fig. 1. The molecular structure of *cis*-(OC)$_4$Mo[P(NHPh)$_2$]$_2$-NPh. Hydrogen atoms are omitted for clarity and only one of two positions of disorder for Ph3, A, is shown. Primed atoms are related to unprimed atoms by the appropriate symmetry operations. Selected bond distances (Å) are: MO–P, 2.48(1); P–N(1), 1.71(2); P–N2, 1.65(2); P–N3, 1.66(3); Mo–Cl, 1.94(5) and Cl–O1, 1.15(4). Selected bond angles (deg) are: P–Mo–P′, 65.8(4); Mo–P–N1, 95.2(7); P–N1–P′, 104(2); Mo–P–N2, 123(1); Mo–P–N3, 126(1); N2–P–N3, 100(1); N1–P–N3, 110(1); and N1–P–N2, 99(1).

Unambiguous structural characterization of *2*·½(C$_6$H$_6$) 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

0020-1693/82/0000-0000/$02.75

in the PhN[P(NHPh)$_2$]$_2$ unit [2] are affected slightly by coordination to the Mo(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 *cis*-(OC)$_4$Mo·nor–(PhNH)$_3$P reaction mixture shows that formation of *2* is preceeded 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 *cis*-(OC)$_4$Mo-(PCl$_3$)$_2$–PhNH$_2$ reaction. Because *3*, upon removal of PhNH$_2$ undergoes conversion to *2, 3* is characterized tentatively as *cis*-(OC)$_4$Mo[P(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 *cis*-(OC)$_4$Mo(PCl$_3$)$_2$ or primary aminophosphines with *cis*-(OC)$_4$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 Rn(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.

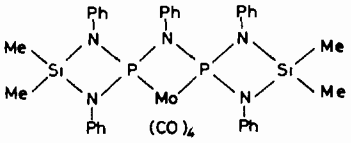


(4)

3

2

Preliminary experiments indicate *2* is a species upon which novel derivatization can be based. Reaction of *2* with Me$_2$SiCl$_2$ in the presence of excess Et$_3$N yields a product characterized tentatively as *4*. In contrast, reaction of Me$_2$SiCl$_2$ with uncoordinated PhN[P(NHPh)]$_2$ in the presence of excess Et$_3$N appears to yield only intractable products.



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Acknowledgements

Support of this work by National Science Foundation Grants CHE-7604290 and CHE-790945 and the University of Colorado Computing Center is gratefully acknowledged.

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6 Satisfactory elemental analytical data for *2*·½(C$_7$H$_8$) were obtained.

7 The crystals of *2*·½(C$_6$H$_6$) are hexagonal, space group P6$_1$22, with 6 molecules in a unit cell of dimensions *a* = 15.606(4), *b* = 15.606(4), *and c* = 28.721(4) Å.