Synthesis and Structure of a *trans*-Molybdenum Complex with Two Different Phosphine Ligands: *trans*-$Mo(CO)_4(PPh_2NH_2)(PPh_2F)$

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Kraihanzel and coworkers have reported that the reaction of *cis*-$Mo(CO)_4(PPh_2NH_2)_2$ with boron trifluoride etherate resulted in deamination and formation of a PNP chelate ring in the product, $\overline{Mo(CO)_4(Ph_2PNHPPh_2)}$ [1]. Similar formation of PNP groups from the *trans*-isomer may generate linked polymetallic complexes. Instead we have found that the same reaction using *trans*-$Mo(CO)_4(PPh_2NH_2)_2$ yielded the fluoride-exchanged product, *trans*-$Mo(CO)_4(PPh_2NH_2)(PPh_2F)$ (**1**), as the only major isolated product. Structural data of *trans*-metal carbonyl complexes are relatively rare, especially those with two different phosphine ligands. Determination of the structure of **1** therefore allows a direct comparison of the coordination of an aminophosphine *versus* a fluorophosphine within the same complex.

Results and Discussion

Addition of two equivalents of $BF_3 \cdot OEt_2$ to *trans*-$Mo(CO)_4(PPh_2NH_2)_2$ in THF gave a cloudy solution after 1 h. Workup of the reaction mixture afforded a 50% yield of a tan powder, complex **1**[†]. It exhibited proton resonances at 7.73(m) and 2.90(s) ppm; ^{31}P signals at 201.3 ppm (doublet of doublets, $^1J_{PF} = 868$ Hz, $^2J_{PP} = 76$ Hz) and 73.5 ppm (doublet of doublets, $^3J_{PF} = 2$ Hz) as well as ^{19}F resonance at 139.7 ppm (referenced to external trifluoracetic anhydride, doublet with $^1J_{PF} = 867$ Hz). Its infrared spectrum in the carbonyl stretching region included absorptions at 2025(w), 1969(w), and 1916(s) cm^{-1} (CH_2Cl_2 solution). N–H stretches are at 3458 and 3349 cm^{-1} (KBr). An analogous product can be obtained from *trans*-$Mo(CO)_4(PPh_2NMeH)_2$ and $BF_3 \cdot OEt_2$.[≠]

Colorless rhombohedral plates of **1** were grown from warm ether/hexane solutions. Crystal data: $MoP_2FO_4NC_{28}H_{22}$, space group monoclinic ($P2_1/c$), $a = 14.837(1)$, $b = 10.935(1)$, $c = 17.391(2)$ Å, $\beta = 104.74(1)°$, $Z = 4$. The structure was solved by application of MULTAN using 4286 significant reflections and refined to a final R_F value of 0.039 and R_{WF} value of 0.030. The amino hydrogens were not located. The molecular structure is shown in Fig. 1. Important bond lengths and angles are listed in Table I. The metal–phosphorus bond of PPh_2F at 2.414(1) Å is 0.06 Å shorter than the one to PPh_2NH_2 at 2.471(1) Å, consistent with the superior metal bonding ability of the fluorophosphine. Average P–phenyl distance for the PPh_2F ligand is 1.811(3) Å as compared to 1.835(2) Å for PPh_2NH_2, indicative of more phenyl-to-phosphorus donation in the former. The metal carbonyl distances range from 2.005(4) to 2.035(4) Å. A slight deviation from linearity of the *trans*-ligands is indicated

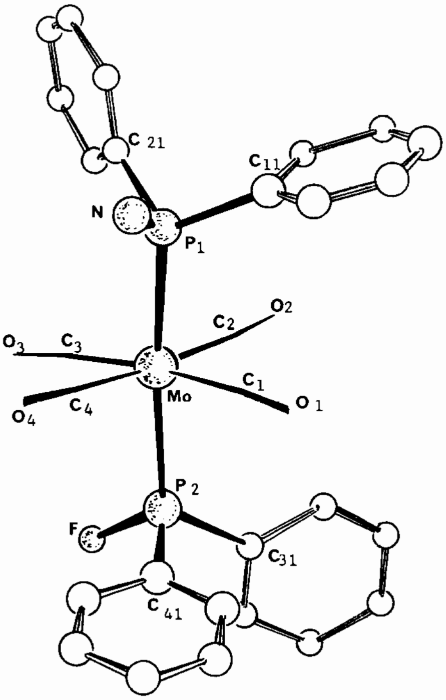

Fig. 1. Molecular structure of *trans*-$Mo(CO)_4(PPh_2NH_2)(PPh_2F)$, (**1**).

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[†] *Anal.* Calc. for $C_{28}H_{22}FMoNO_4P_2$: C, 54.83; H, 3.62; N, 2.28. Found: C, 55.14; H, 3.48; N, 2.28%.

[≠] A 65% yield of *trans*-$Mo(CO)_4(PPh_2NHMe)(PPh_2F)$ can be similarly obtained. Spectral data: IR(CO) 2025(w), 1976(w), 1930(w), 1918(s) cm^{-1}; ^{31}P NMR 207.2 (doublet of doublets, $^1J_{PF} = 859$, $^2J_{PP} = 73$ Hz) and 89.4 ($^3J_{PF} = 2$ Hz). *Anal.* Calc. for $C_{29}H_{24}FMoNO_4P_2$: C, 55.52; H, 3.86; N, 2.23. Found: C, 55.28; H, 3.87; N, 2.26%.

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TABLE I. Bond Distances (Å) and Angles (°)[a]

Bond distances			
Mo–P(1)	2.471(1)	P(1)–N	1.671(3)
Mo–P(2)	2.414(1)	P(1)–C(11)	1.838(4)
Mo–C(1)	2.023(4)	P(1)–C(21)	1.832(4)
Mo–C(2)	2.019(4)	P(2)–F	1.614(2)
Mo–C(3)	2.035(4)	P(2)–C(31)	1.816(4)
Mo–C(4)	2.005(4)	P(2)–C(41)	1.806(4)
Bond angles			
P(1)–Mo–P(2)	173.1(1)	C(1)–Mo–C(2)	97.2(2)
P(1)–Mo–C(1)	87.4(1)	C(2)–Mo–C(3)	88.1(2)
P(1)–Mo–C(2)	87.1(1)	C(3)–Mo–C(4)	86.5(2)
P(1)–Mo–C(3)	97.9(1)	C(4)–Mo–C(1)	88.5(2)
P(1)–Mo–C(4)	90.1(1)	Mo–P(1)–N	113.1(1)
		Mo–P(2)–F	114.8(1)

[a] Standard deviations are in parentheses.

by the P–Mo–P angle of 173.1(1)°. Intermolecular hydrogen-bonding is not observed in the cell packing.

The different reaction courses of *cis*- and *trans*-$Mo(CO)_4(PPh_2NH_2)_2$ with boron trifluoride can be rationalized. Initial coordination of BF_3 to the amino group in both cases seems reasonable. Subsequent fluoride exchange has precedence in the thermally unstable N-coordinated adduct of BF_3 with $PF_2(NMe_2)$ to give $(Me_2NBF_2)_2$ and PF_3 [2].

$$PF_2(NMe_2) + BF_3 \longrightarrow PF_2(NMe_2 \cdot BF_3) \longrightarrow PF_3 + 0.5(NMe_2BF_2)_2$$

Greenwood and Robinson have also noted a fluoride exchange in the adducts of BF_3 with amino(trifluoromethyl)phosphines [3]. Therefore it is likely that a similar process generated complex **1**. By contrast, the proximity of a second amino group in the *cis*-adduct apparently led to intramolecular nucleophilic displacement at P instead, resulting in ring closure and probable loss of $BF_3 \cdot NH_3$.

References

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