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The Photochemical Substitution Reactions of [Mo(CO)$_4$(dppe)] with PF$_3$, Me$_2$NPF$_2$ and MeN(PF$_2$)$_2$

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The thermal substitution reactions of [(chelate)-Mo(CO)$_4$] complexes, where 'chelate' = N–N [1–3], P–P [3–5], S–S [3], and N–P [3] bidentate ligands, with various Lewis bases L = amine, phosphine and phosphite have been described. These reactions give products, and follow kinetics that depend upon the nature of L and the chelating ligand. The postulated primary steps include: (i) unimolecular dissociation of CO [6, 7], (ii) nucleophilic attack by L on [(chelate)Mo(CO)$_4$] [1, 7], and (iii) reversible dissociation of one end of the chelating ligand [7]. Products of the type [(chelate)Mo(CO)$_3$L], [Mo(CO)$_4$-L$_2$] and [Mo(CO)$_3$L$_3$] have been isolated from these reactions.

In this paper we report our studies of the photochemical reactions of [(Mo(CO)$_4$(dppe)] with the ligands PF$_3$, Me$_2$NPF$_2$ and MeN(PF$_2$)$_2$, and the isolation of the new compounds [Mo(PF$_3$)$_4$(dppe)], [Mo(Me$_2$NPF$_2$)$_6$] and [Mo(CO)$_2$(dppe)(MeN(PF$_2$)$_2$)]. Comparative studies of the reactions of P(OMe)$_3$ and dppe with [Mo(CO)$_4$(dppe)] were also done in order to clarify the nature of some of the reaction intermediates.

Discussion

Under thermal conditions, [Mo(CO)$_4$(dppe)] is known to resist attack by nucleophiles, and elevated temperatures that facilitate CO dissociation are required in order to effect substitution [3, 5]. Dobson [5] has postulated that strong π-accepting phosphites are better able to compete with CO than Ph$_3$P, Ph$_3$Sb and n-octylamine. In these cases the reaction kinetics indicate a reversible, rate-determining dissociation of CO to give a five-coordinate intermediate. On the basis of π-bonding and 'site preference' [8] considerations, it is proposed that a CO group *cis* to dppe is preferentially lost. In studies of the substitution reactions of [Mo(CO)$_4$(P–en)] (P–en = H$_2$PCH$_2$CH$_2$-PH$_2$), products of the type *fac*- and *mer*-[Mo(CO)$_3$-(P–en)L], and [Mo(CO)$_2$(P–en)L$_2$] have been characterized [4].

We have examined the reactions of [Mo(CO)$_4$-(dppe)] with various proportions of ligands L = PF$_3$, Me$_2$NPF$_2$, MeN(PF$_2$)$_2$, (MeO)$_3$P and dppe in solution in THF and in toluene, under photochemical conditions. The progress of the reactions, in pyrex vessels, were monitored by ^{31}P NMR spectroscopy, and by intermittently measuring the amount of evolved carbon monoxide. In all cases, a yellow to amber color rapidly developed, and ^{31}P NMR signals attributable to *fac*-[Mo(CO)$_3$(dppe)L] appeared. Evidence for the latter was based upon: (i) a doublet (L = P(OMe)$_3$) or a doublet of multiplets (L = fluorine containing ligands), slightly upfield relative to δ ^{31}P ([Mo(CO)$_4$(dppe)]), due to the equivalent ^{31}P nuclei of dppe coupled with the spin 1/2 phosphorus nucleus of the L ligand ($J_{\mathrm{P-P}} \cong 30$–$35$ Hz); and (ii) a signal, downfield from 'free' L, attributable to the coordinated L ligand. This signal, in the cases L = PF$_3$ and P(OMe)$_3$, was split into a triplet by coupling with the equivalent ^{31}P nuclei of dppe, the coupling constants ($J \approx 30$–35 Hz) being typical for a *fac* configuration [9–11]. The ^{31}P NMR spectra of coordinated Me$_2$NPF$_2$ and MeN(PF$_2$)$_2$ in *fac*-[Mo(CO)$_3$-(dppe)L] showed complex coupling features [12–14] which were not sufficiently resolved to provide coupling constant data.

In two cases, *viz.* L = Me$_2$NPF$_2$ and P(OMe)$_3$, ^{31}P signals attributable to monodentate and to free dppe were also observed, in addition to those due to [Mo(CO)$_3$(dppe)L]. These observations provide direct evidence of the opening of the chelate ring prior to its displacement. In the photolysis of [Mo(CO)$_4$-(dppe)] and excess dppe, ^{31}P NMR evidence indicated the initial formation of *fac*-[Mo(CO)$_3$(dppe)L] (L = monodentate dppe) prior to ring closure to give [Mo(CO)$_2$(dppe)$_2$].

The monodentate MeN(PF$_2$)$_2$ ligand in *fac*-[Mo(CO)$_3$(dppe)(MeN(PF$_2$)$_2$)] showed two ^{31}P resonances, as triplets ($J_{\mathrm{P-F}} \approx 1100$ Hz) of multiplets corresponding to the coordinated (δ ^{31}P = 174 ppm, $\Delta = 7$) and to the free (δ ^{31}P = 111 ppm, $\Delta = 0$) phosphorus centres. The photolysis of [Mo(CO)$_4$-(dppe)] and MeN(PF$_2$)$_2$ was monitored until ≈ 2 equivalents of CO had been collected. The solvent was removed, leaving off-white crystals of [Mo(CO)$_2$-(dppe)(MeN(PF$_2$)$_2$)]. The mass spectrum of this product showed the parent ion (P(^{98}Mo)$_{\mathrm{obs.}}$ = 719, P$_{\mathrm{calcd.}}$ = 719) and major species corresponding to the sequential loss of two CO groups, followed by the loss of MeN(PF$_2$)$_2$. A very weak signal due to Mo(CO)-(dppe) was observed.

During continued photolysis, a *fac*- to *mer*-isomerization of [Mo(CO)$_3$(dppe)L] complexes was apparent, as evidenced by (iii) the appearance of two sets of ^{31}P signals, attributable to inequivalent P nuclei of dppe, one being *trans* and one *cis* to L. The $J_{\mathrm{P-P}}$ coupling constants were 130–140 Hz and 30–35 Hz, respectively, values that are typical for the assigned con-

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figurations [9–11]. The former signal was 8–10 ppm downfield, and the latter 1–2 ppm downfield from the ^{31}P signals of [$Mo(CO)_4$(dppe)]; and (iv), a downfield shift of the ^{31}P signal due to the L ligand. In one case (L = $P(OMe)_3$), this signal was resolved into a doublet of doublets, arising from coupling with the *trans* ($J_{P-P} \cong 130$ Hz) and the *cis* ($J_{P-P} \cong 35$ Hz) phosphorus nuclei of dppe. The reported derivative *mer*-[$Mo(CO)_3$(dppe)($P(OEt)_3$)], prepared by thermal means, also shows the two sets of ^{31}P signals described in (iii) and (iv) above [10].

In addition to the above noted *fac–mer*-isomerization of [$Mo(CO)_3$(dppe)L] the appearance of signals due to further photolytic substitution products was noted. For L = PF_3, the mixed products [$Mo(CO)_x$-$(PF_3)_{4-x}$(dppe)] were observed but were not separated. Accordingly a mixture of [$Mo(CO)_4$(dppe)] and a 10-fold excess of PF_3 was photolysed (in pyrex) for 20 hours. Most of the CO (> 90%) was eliminated. Upon removal of the volatile components under vacuum, white crystals of [$Mo(PF_3)_4$(dppe)], slightly contaminated with [$Mo(CO)(PF_3)_3$(dppe)], were obtained. The former was purified by recrystallization from dichloromethane. The mass spectrum of [$Mo(PF_3)_4$(dppe)] showed the parent ion ($P(^{98}Mo)_{obs} = 848$, $P_{calcd} = 848$) and species corresponding to the sequential loss of four PF_3 groups, in patterns consistent with the isotopic constitution of Mo. The base peak corresponded to Mo(dppe). The same base peak was observed in the mass spectrum of [$Mo(CO)_4$-(dppe)]. The next lower mass fragment corresponded to $Mo(PPh_2)_2$, representing the extrusion of the CH_2CH_2 (Mass = 28) moiety. The ^{31}P NMR spectrum of [$Mo(PF_3)_4$(dppe)] consisted of an upfield multiplet, centred at 52 ppm, due to the equivalent P atoms of dppe, and two downfield quartet sets of multiplets corresponding to the two magnetically distinct pairs of PF_3 groups. On the basis that the ^{31}P resonance for the L ligand in *mer*-[$Mo(CO)_3$-(dppe)L] occurs downfield from that of the *fac* isomer, the signals centered at 158 and at 156 ppm may be assigned to the two pairs of PF_3 ligands that are *trans* and *cis*, respectively, to the dppe ligand. Because of numerous spin–spin couplings, all of the above signals were complex and most coupling constants could not be evaluated accurately.

The minor product [$Mo(CO)(PF_3)_3$(dppe)] showed a weak carbonyl vibration at 1913 cm^{-1}, and a mass spectrum consisting of the parent ion, together with species corresponding to the stepwise loss of three PF_3 groups, followed by the loss of the unique carbonyl group. The base peak again corresponded to Mo(dppe).

The photolysis of [$Mo(CO)_4$(dppe) and Me_2NPF_2 (1:6 molar ratio) lead to the complete elimination of dppe and the formation of an inseparable mixture of products. A sample, which was recrystallized from CH_2Cl_2/hexane, gave a mass spectrum showing the parent ions of [$Mo(CO)(Me_2NPF_2)_5$], [$Mo(CO)_2$-$(Me_2NPF_2)_4$] and [$Mo(CO)_3(Me_2NPF_2)_3$]. Sequential losses of Me_2NPF_2 and CO were evident, and the strongest signal was due to $Mo(Me_2NPF_2)_2$.

A mixture of [$Mo(CO)_6$] and Me_2NPF_2 (1:10 molar ratio) in toluene was photolysed for 15 hours, while evolved CO was removed at intervals. The complex [$Mo(Me_2NPF_2)_6$] was isolated in high yield (> 90%). The mass spectrum of the recrystallized product showed the parent ion ($P(^{98}Mo)_{obs.} = 776$; $P_{calcd.} = 776$) and strong signals due to Mo-$(Me_2NPF_2)_x$ (x = 1 – 5). In addition, weak signals corresponding to the loss of one fluorine atom, and to the loss of one Me_2N group from the Mo-$(Me_2NPF_2)_x$ fragments were observed. The ^{31}P NMR spectrum of [$Mo(Me_2NPF_2)_6$] showed a triplet ($J_{P-F} = 1080$ Hz) of multiplets, centered at 145 ppm.

Conclusions

The photochemical reaction of [$Mo(CO)_4$(dppe)] with the ligands L = PF_3, Me_2NPF_2, $MeN(PF_2)_2$, $P(OMe)_3$ and dppe initially gives *fac*-[$Mo(CO)_3$-(dppe)L], in agreement with the findings of Dobson *et al.* [15] that [$Mo(CO)_4$(dppe)] undergoes substitution via loss of one of the trans pair of carbonyl groups, the five-coordinate [$Mo(CO)_3$(dppe)] intermediate being square-pyramidal and non-fluxional at ambient temperature. The *fac* products readily isomerize, under photochemical conditions, to the *mer* configuration. By comparison, *fac*-[$Mo(CO)_3$-(dppe)(PPh_3)] is stable at room temperature but isomerizes at 125 °C, whereas *fac*-[$Mo(CO)_3$(dppe)-($C_6H_{11}NH_2$)] is stable even at elevated temperatures [15].

The complexes [$Mo(CO)_3$(dppe)L] react further with excess L in two different ways. For L = PF_3 and $MeN(PF_2)_2$, carbonyl substitution leads to [$Mo(CO)_x$(dppe)$(PF_3)_{4-x}$] and [$Mo(CO)_2$(dppe)-($MeN(PF_2)_2$)]. With L = Me_2NPF_2 and $P(OMe)_3$, however, displacement of dppe as well as CO occurred, giving products of the type [$Mo(CO)_x(L)_{6-x}$]. Thus, the first two ligands, which exhibit strong π-bonding properties [16], compete only with CO, whereas the strongly σ-donating ligands Me_2NPF_2 and $P(OMe)_3$ compete with the σ-donating dppe ligand as well. Likewise, in aminemetalcarbonyl complexes, ligand lability increases with increase in basicity of the amine moiety [2].

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