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Ligand effects in the substitution chemistry of *cis*-bis(piperidine)tetracarbonylmolybdenum(O). A molybdenum-95 NMR study

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Abstract—Molybdenum-95 NMR chemical shifts are reported for a series of Mo(O) compounds of the type $Mo(CO)_4(pip)_{2-n}L_n$ ($n = 1, 2$; L = substituted pyridine ligands). The $\delta(^{95}Mo)$ values correlate well with the pK_a values for the substituted pyridines; for the $n = 1$ series, $\delta(^{95}Mo)$ ranges from -1053 ppm ($pK_a = 1.86$ for 4-CN) to -1120 ppm ($pK_a = 9.61$ for 4-NMe_2). The effects of solvent polarity and some *in situ* reactivity studies are described and the nature of the Mo–L bond compared to that with piperidine and some other ligands is discussed.

INTRODUCTION

METAL NMR spectroscopy has developed into a powerful tool for probing structures and reactivities of coordination compounds in solution. Our interest has focused on the utility of molybdenum-95 NMR spectroscopy due to the large chemical shift scale of over 7000 ppm that is known for the Mo-95 nucleus. There is potential for detecting minor variations in electron density at the molybdenum nucleus with subtle changes in electronic and steric effects operating within a series of closely related compounds [1]. Several other applications for ^{95}Mo NMR have also been reviewed [1–3] and recently, it has been demonstrated that *in situ* ^{95}Mo NMR can be very effective for investigating complicated reaction mixtures [4, 5].

In this paper, we report our results for a systematic *in situ* ^{95}Mo NMR study of ligand effects in some substitution chemistry of $Mo(CO)_4(pip)_2$ (pip = piperidine). This work follows upon our earlier investigation of a series of mono-substituted compounds, $Mo(CO)_5L$ (L = substituted pyridine) [6], wherein we found that the molybdenum nucleus becomes increasingly more shielded as the σ-donicity of L increases, concomitant with decreasing values for $\nu(CO)$ for carbonyls *trans* to L [7]. We interpret these trends to mean that strong σ-donors promote strengthening of the *trans* Mo–C bonds via a synergistic mechanism. We now consider the applicability of this rationalization to the related series of compounds, $Mo(CO)_4(pip)_{2-n}L_n$ (L = substituted pyridine), and include extensions to other ligands such as CO, $NCCH_3$ and triarylphosphines ($P(Ar)_3$).

EXPERIMENTAL

$Mo(CO)_4(pip)_2$ was isolated in good yields (95–97%) from reaction mixtures of $Mo(CO)_6$ and piperidine (1:6, mole:mole) in heptane after reflux (4–6 h) under dinitrogen atmospheres [8]. Although this compound is reasonably stable as a solid, dimethylformamide (DMF) stock solutions proved to be unstable over relatively short periods of time (changing in colour from yellow to dark yellow to brown). Thus, samples for ^{95}Mo NMR spectroscopy were prepared just prior to NMR analysis. Typically, $Mo(CO)_4(pip)_2$ (0.2 g, 0.53 mmol) was dissolved in DMF (2.5 cm^3) in a 10 mm OD NMR tube, and the appropriate ligand was added directly, in stoichiometric amounts and at ambient temperatures. Care was taken to ensure that time lapses, from sample preparation to sample analysis, were equal for each ligand so that relative measures of the extent of reaction could be based on signal to noise ratio achieved for a fixed number of transients collected.

The ^{95}Mo NMR spectra were acquired on a Bruker WH-400 spectrometer operating in the pulsed FT mode at 26.0785 MHz and at ambient temperatures (297 ± 2 K). Chemical shifts are

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Table 1. pK_a and ^{95}Mo NMR data for *cis*-$Mo(CO)_4(pip)_{2-n}L_n$

L	pK_a*	δ ^{95}Mo (ppm) ($\Delta\nu_{1/2}$, Hz) $n=1$	$n=2$
4-cyanopyridine	1.86	−1053 (110)	no rxn†
3-chloropyridine	2.81	−1066 (150)	no rxn†
3-bromopyridine	2.85	−1062 (180)	no rxn†
pyridine	5.25	−1079 (120)	−1060 (140)‡
4-phenylpyridine	5.35	−1079 (150)	−1063 (310)‡
4-benzylpyridine	5.59	−1083 (140)	−1070 (300)‡
3-methylpyridine	5.68	−1079 (140)	−1062 (150)
4-methylpyridine	5.99	−1087 (140)	−1074 (120)
4-t-butylpyridine	5.99	−1090 (320)	−1077 (220)
4-ethylpyridine	6.03	−1084 (120)	−1071 (140)
2,6-dimethylpyridine	6.78	no rxn†	no rxn†
2,4,6-trimethylpyridine	7.56	−1084 (150)	−1067 (150)
4-dimethylaminopyridine	9.61	−1120 (140)	−1369 (130)§
piperidine	11.2	−1093 (80)	−1093 (80)
CO	—	−1457 (60)	no rxn
$NCCH_3$	—	−1213 (60)	−1304 (70)
$NCCH_2CH_3$	—	−1213 (60)	−1305 (70)
$P(p\text{-}C_6H_4Cl)_3$	1.03	−1314 (270)‡‖	no rxn†
PPh_3	2.73	−1322 (270)‡‖	no rxn†
$P(p\text{-}C_6H_4MeO)_3$	4.57	−1327 (480)‡‖	no rxn†
1/2 dipy	—	—	−1189 (120)¶

* Values for nitrogen donors calculated from data in Ref. [9]; values for phosphorus donors are from Ref. [10].

† No reaction.

‡ Requires excess ligand.

§ Assigned as *trans*-$Mo(CO)_4(L)_2$, see text.

‖ $^1J(^{95}Mo-^{31}P)$ unresolved.

¶ −1190 (110 Hz) ppm in Ref. [12].

relative to aqueous alkaline (pH 11) 2 M K_2MoO_4 (set at 0.00 ppm) and are considered to be accurate to ± 1 ppm. In several cases, sample integrity was subsequently verified by IR spectroscopy (Nujol Mull) on a Nicolet 20 DXC FT spectrophotometer (2600–200 cm^{-1}) with a resolution of 2 cm^{-1}.

Results and Discussion

Many of the species to be discussed here (see Table 1) have been, or can be, synthesized directly from $Mo(CO)_6$ [4, 8] but synthesis usually requires reflux conditions. That is, $Mo(CO)_6$ does not readily undergo substitution chemistry at ambient temperatures whereas *cis*-$Mo(CO)_4(pip)_2$ does undergo both mono- and bis-substitution of the piperidine ligands. The occurrence and/or extent of bis-substitution, however, are very dependent upon the nature of the incoming ligand, L (*vide infra*). Substitution of CO ligands and/or coordination of a third L were not observed.

Dimethylformamide solutions of $Mo(CO)_6$, *cis*-$Mo(CO)_4(pip)_2$ and *cis*-$Mo(CO)_4(pip)_{2-n}L_n$ ($n=1,2$) tend to be colourless, yellow and red, respectively. These colour changes upon substitution of pip for CO and subsequent substitution of L for pip correspond to increased deshielding of the molybdenum nucleus and this can be perhaps best explained by reference to the Ramsey expression Eqn (1) [11]. For quadrupolar nuclei, such as ^{95}Mo ($I=5/2$), the paramagnetic shielding term dominates in determining the observed chemical shift and can be expressed in a simplified form [Eqn (2)].

$$\delta = \delta_{dia} + \delta_{para} \quad (1)$$

$$\delta_{para} = -K\Delta E^{-1}\langle r^{-3}\rangle_{4d}k^2. \quad (2)$$

Either the "spectrochemical" or "nephelauxetic" components of the paramagnetic term δ_{para} can be dominant, as well documented [1], and one can only tentatively suggest their relative importance. It is clear, however, that the Mo atom will be more shielded by a strong field ligand (large ΔE) and by a more polarizable, covalently bound ligand (decreased value of $\langle r^{-3}\rangle_{4d}k^2$). For the above related series of complexes the predominant term in Eqn (2) appears to be ΔE. This refers to the octahedral ligand field splitting energy and approximates the HOMO–LUMO energy gap for the Mo 4*d* orbitals. Replacement of CO in $Mo(CO)_6$ with a ligand lower in the spectrochemical series, such as pip or py, leads to a smaller ΔE term and consequently, a higher absolute magnitude for δ_{para}. Since the latter term is negative in sign, an increased magnitude corresponds to deshielding of the molybdenum nucleus. Thus, one might expect good π-acceptor and strong σ-donor ligands to promote shielding. These expectations are not contradicted by the data in Table 1.

If one considers ligand basicity, as represented by pK_a, to be a reasonable relative measure of relative σ-donicity, then for a given series of ligands (see Table 1) shielding is observed to increase with increasing pK_a. It should be pointed out here that pK_a values for pip, $P(Ar)_3$ and the substituted pyridines are measured and/or derived in different ways so that care must be taken when these different types of ligands are to be compared. For example, despite lower pK_a values mesured for $P(Ar)_3$ relative to the nitrogen donors, the latter, as expected [12, 13], are more deshielding. Theoretically, pyridine ligands are capable of π-acid behaviour via the π^* orbitals of their aromatic systems [14], but the consensus is that this type of behaviour is essentially negligible [15]. Thus, we suggest that the pyridine ligands act as σ-donors only and that the relatively higher degree of shielding observed for the phosphine complexes are an indication that there is some degree of Mo–P $d\pi$–$d\pi$ backbonding operating in these complexes. Alternatively, the greater shielding may be due, at least partially, to the greater polarizability of phosphorus ligands as compared to nitrogen ligands. The difficulty of separating the influence of the components of Eqn (2) in attributing changes in chemical shifts, for a series such as those in Table 1, should always be borne in mind.

The substituted pyridines, however, do substitute pip much more readily than $P(Ar)_3$ does. In fact, even upon warming of the reaction mixtures (60°C, 1 h), secondary substitution of pip is not observed for the $P(Ar)_3$ ligands and this is consistent with an earlier report for substitution of py by phosphine ligands in *cis*-$W(CO)_4(py)_2$ [16]. It was found, in this case, that the first py is substituted at 40°C but secondary substitution requires much more rigorous conditions. Clearly, the non-planarity and greater steric bulk of $P(Ar)_3$, relative to the pyridine ligands, are inhibitory factors in the formation of *cis*-$Mo(CO)_4(pip)_{2-n}L_n$ ($L = P(Ar)_3$). Finally, in terms of differences observed, in the case of pyridine ligands, piperidine substitution tends to be more facile as ligand pK_a increases whereas the opposite trend is observed for $P(Ar)_3$. The difference in behaviour cannot be explained easily on the basis of differing ligand geometries and/or steric properties.

The line widths observed are greater for the $P(Ar)_3$-containing species due to relatively lower symmetry at Mo [1] but also to unresolved higher coupling to molybdenum-95 ($^1J(^{95}Mo–^{31}P) \approx 125–140$ Hz [4, 13]. In general, the broader resonance line widths observed for the other complexes compared to those measured for the L = CO and CH_3CN cases doubtless reflects the occurrence of greater asymmetry and electric field gradients at the molybdenum nucleus [1, 4] The effect of another important parameter that causes broadening [1, 4], the molecular correlation time, can be seen in the values of $\Delta\nu_{1/2}$ for the complexes of 4-t-butylpyridine compared to those of 4-methylpyridine.

For a given substituted pyridine, with the exception of 4-dimethylaminopyridine (*vide infra*), the mono-substituted species is more shielded than the bis-substituted species. Plots for chemical shift versus ligand pK_a show that shielding increases with increasing ligand pK_a in a fairly linear fashion and that this effect is more pronounced (i.e. steeper gradient) for the mono-substituted species. The chemical shifts for the mono-substituted

species are consistently 2–5 ppm more shielded than positions expected on the basis of averages of observed chemical shifts for the corresponding bis-substituted species and *cis*-$Mo(CO)_4(pip)_2$. These results indicate that stronger σ-donors do lead to shielding of the molybdenum nucleus and that piperidine is generally a better σ-donor (or higher in the spectrochemical series) than the substituted pyridines. Furthermore, the data in Table 1 indicate that the ^{95}Mo chemical shift is sensitive to the position of the substituent(s) present on pyridine. This was not the case for the analogous species, $Mo(CO)_5L$ (L = substituted pyridine) [6].

Clearly, the introduction of *ortho* substituents introduces steric effects. That is, the lack of reaction observed for 2,6-dimethylpyridine can be ascribed to steric inhibition as the less crowded species, *trans*-$Mo(CO)_4$(2,6-dimethylpyridine)$_2$ ($\delta^{95}Mo = -1351$ ($\Delta\nu_{1/2} = 10$ Hz)), is known [4]. Nevertheless, the equally bulky but more basic ligand, 2,4,6-trimethylpyridine, forms both the mono- and bis-substituted *cis* species quite readily.

Generally, disubstituted hexacoordinate compounds of molybdenum carbonyl with other non- or lesser π-acid ligands have *cis*-geometry [4, 15e] which is thermodynamically favoured over the corresponding *trans*-geometry [15e, 17] despite opposite expectations on the basis of steric factors [16, 18]. The concept of synergism [19] can be invoked here. That is, for compounds such as $Mo(CO)_6$, the strong π-acid CO ligands relieve charge build-up on the Mo centre. As CO is replaced by a ligand, L, a competition for backbonding with the filled Mo 4*d* orbitals arises between L and CO *trans* to L. If L is a poor π-acid or a σ-donor only, then it will compete poorly and the Mo–CO bond *trans* to L will be strengthened. Subsequent substitution by a second L will be directed *cis* to minimize the number of mutually *trans* CO ligands [20].

Piperidine is a non π-acid but a very good σ-donor. Our attempts, during this study, to form *trans*-$Mo(CO)_4(pip)_2$ were unsuccessful. Nevertheless, the Mo–N bonds formed by piperidine are relatively strong. Bubbling of a DMF solution of *cis*-$Mo(CO)_4(pip)_2$ with CO (20 min) leads to $Mo(CO)_5$(pip), but no further substitution occurs at ambient temperatures. This is consistent with an earlier study [14] for formation of $Mo(CO)_6$ from reaction of CO with $Mo(CO)_5$ (amine). It was found that Mo–N bond cleavage is the rate-determining step and that the rate of formation of $Mo(CO)_6$ decreases with increasing amine pK_a. The relatively facile formation of *trans*-$Mo(CO)_4$(4-dimethylaminopyridine)$_2$ suggests that 4-dimethylaminopyridine is a stronger σ-donor than piperidine and that very strong σ-donors can stabilize *trans*-isomers, even in the absence of steric effects.

The chemical shifts observed for *cis*-$Mo(CO)_4(pip)_{2-n}(NCR)_n$ (R = CH_3, CH_2CH_3) are significantly shielded relative to analogous substituted pyridine species. This is in agreement with $NCCH_3$ being higher than pyridine in the spectrochemical series. In any case, that the Mo–$NCCH_3$ bond is fairly strong relative to Mo–CO bonds has been borne out by thermochemical analyses [21]. Other thermochemical studies [22] have indicated that in $Mo(CO)_{6-n}L_n$ ($n = 1$–3), the Mo–N bond for L = pip is appreciably stronger than that for L = py. Thus, it could be inferred that increased shielding of the molybdenum nucleus corresponds to increased Mo–N strength. Also, for all the species in Table 1, one might suggest a spectrochemical series that follows the order, py < pip < dipy < $NCCH_3$ < $P(Ar)_3$ < CO. It should be mentioned, however, that the shielding observed for *cis*-$Mo(CO)_4$(dipy) relative to *cis*-$Mo(CO)_4(py)_2$ can also be at least partially ascribed to a chelate ring effect (~120 ppm) active for the former compound [23].

Finally, if a synergistic mechanism is active, then one would expect net molecular dipole moments to increase as $Mo(CO)_6 \ll Mo(CO)_5(pip) < Mo(CO)_4(pip)_2$. The data in Table 2, for solvents listed in order of increasing dielectric constant, are consistent in that as CO is progressively substituted by pip, solubility in low polarity solvents decreases. Furthermore, for either $Mo(CO)_5$pip or $Mo(CO)_4pip_2$, shielding tends to increase with increasing solvent polarity. In contrast, we reported earlier [13] that $Mo(CO)_6$ itself showed the greatest deshielding of the ^{95}Mo nucleus when the solvent was polar (e.g. −1850 for DMF, −1857 for CH_2Cl_2, −1867 for iso-octane). These data do not appear to relate in any meaningful manner with other parameters such as solvent donor and

Table 2. ^{95}Mo NMR data for $Mo(CO)_{6-n}(pip_n)$ in different solvents

Solvent	δ ^{95}Mo (ppm) $n=1$	$n=2$
C_6H_6	−1420	Insoluble
$CHCl_3$	−1420	Insoluble
CH_2Cl_2	−1433	−1075
$(CH_3)_2CO$	−1446	−1077
THF	−1441	−1064
DMF	−1457	−1093
CH_3CN	−1455	—
$(CH_3)_2SO$	−1458	−1097

acceptor numbers (i.e. DN and AN) [24]. The apparent anomalous behaviour for THF might be ascribed to reaction of this solvent wih the substituted compounds. It is worth mentioning that dissolution of $Mo(CO)_{6-n}(pip)_n$ ($n=1,2$) in the related solvent, thiophene, leads to immediate decomposition.

These studies are being extended to the tris-substituted species.

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