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The solution dynamics of adduct formation and electronic communication between ligand and metal core in electron deficient quinoline triosmium clusters‡

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Abstract—The coordination of ammonia and of aliphatic amines (RNH_2(R = Et, n-Bu, s-Bu, t-Bu, cyclohexyl) and Et_2NH) to the electron deficient clusters $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_9H_6N)(\mu\text{-}H)$ (**1**) and $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}XC_9H_5N)(\mu\text{-}H)$ (X = 5-NH_2, **4**; 3-NH_2, **5**; 6-NH_2, **6**; 5-Br, **7**; 5-CH_3, **8**) has been studied. The initially formed adducts of the amines with **1** gradually isomerize to give a mixture of two isomers whose ratio varies with the cluster, the solvent and the amine. Studies of the variation of the isomer ratio with temperature yield ΔH° and ΔS° values for the isomer equilibrium. The primary cause of the change in the isomer ratio is the variation in ΔS° which is rationalized as being due to solvation effects. The overall structure of the two isomers is assigned on the basis of NMR measurements to one where the amine occupies an axial position on the cluster and where the hydride and quinoline ring bridge different edges of the cluster. The equilibrium constant for amine complex formation is primarily determined by the steric bulk of the amine. The amine substituted complex **4** shows absolutely no tendency to coordinate amines and this is ascribed to relief of the electron deficiency at the metal core by the mesomeric effects of the *para*-amino group. The isomeric **5** and **6**, however, do undergo coordination of amines at the metal core. The 5-methyl substituted complex **8** does not complex amine either. Compounds **1**,**4**–**8** all undergo simple protonation with both coordinating (CF_3CO_2H) and non-coordinating acids (HBF_4) to give cationic dihydrido complexes whose solution structures are elucidated by NMR techniques. The chemistry of these electron deficient clusters is compared with related $\mu_3\text{-}\eta^2$ imidoyl complexes and can be understood in terms of the Hammett equation, at least for protonation.

Keywords: Amines; clusters; Osmium; Quinolines.

INTRODUCTION

We recently reported the synthesis and reactivity of a novel class of electron deficient triosmium clusters $Os_3(CO)_9(\mu_3\text{-}\eta$ [2]-$C_9H_6N)(\mu\text{-}H)$ (**1**) from the reaction of quinoline with $Os_3(CO)_{10}(CH_3CN)_2$ followed by thermolysis or photolysis of the initially formed decacarbonyl eq. (1) [1–3]. This type of compound can be synthesized in good yield with a wide range of substituents in the quinoline ring [1, 4].

The reaction of these complexes with soft nucleophiles such as phosphines results in ligand addition at the metal core along with rearrangement eq. (2) [1, 3]. On the other hand, reaction with hydride [1] or carbanions [4] results in nucleophilic attack at the 5-position of the quinoline ring. Subsequent protonation leads to a nucleophilic addition product eq. (3) [4] and hydride abstraction from the intermediate anion effects overall nucleophilic substitution eq. (4) [4]. In light of this diverse reactivity, we thought it would be useful to study the reactivity of **1** with amines

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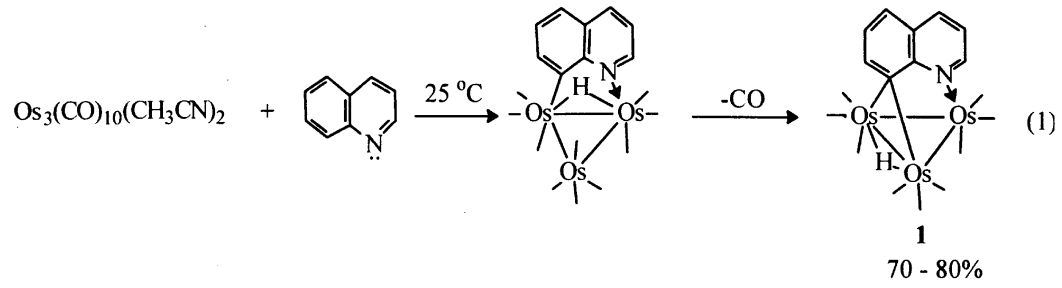
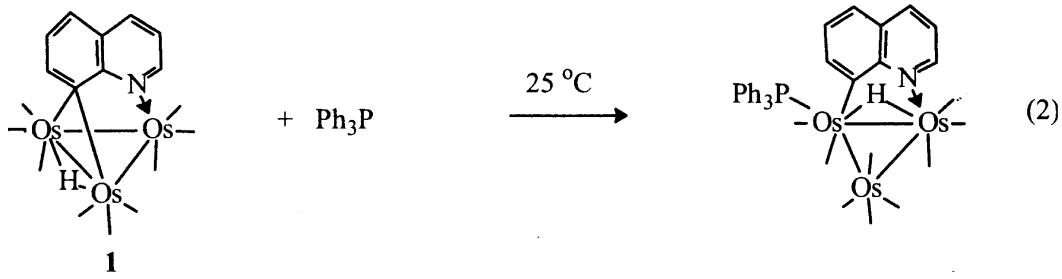
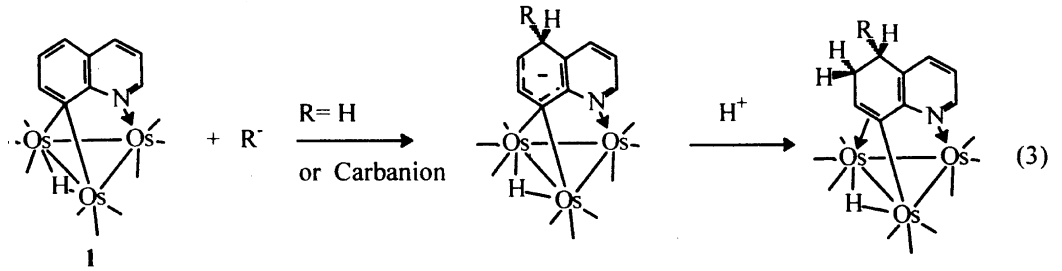
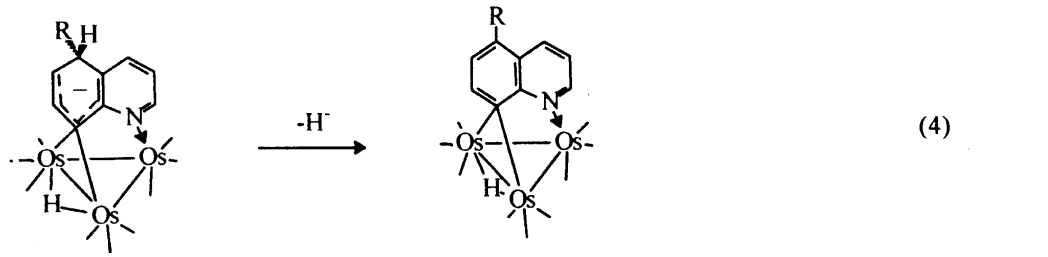
‡ Dedicated, with respect and admiration to Professor Jack Lewis on the occasion of his 70th birthday.





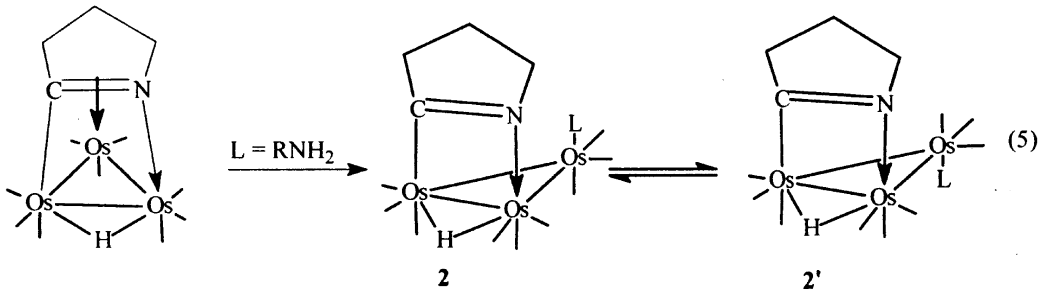


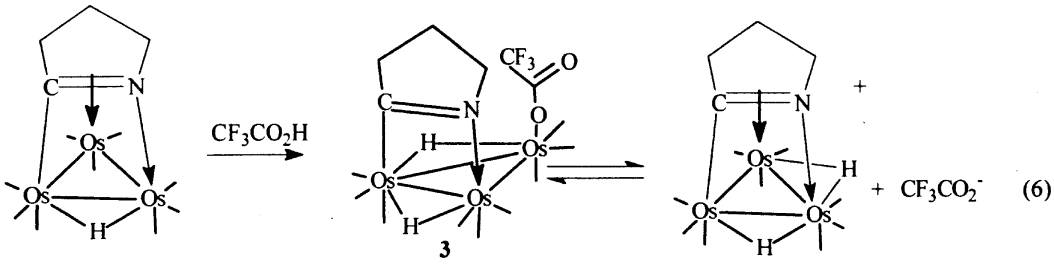


and carboxylic acids which are intermediate in nucleophilicity relative to phosphines and carbanions.

We recently completed detailed studies of the reaction of these ligands with the electron precise, but quite reactive μ_3 imidoyl complexes of the type, $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{=}N(\text{-}CH_2\text{-})_3(\mu\text{-}H)$, where coordination was highly selective for primary amines and where the formation of two axially coordinated isomers, $Os_3(CO)_9(\mu\text{-}\eta^2\text{-}C{=}N(\text{-}CH_2\text{-})_3(\mu\text{-}H)L$ (**2** and **2′**) was observed eq. (5) [5]. The neutral adduct $Os_3(CO)_9(\mu\text{-}\eta^2\text{-}C{=}N(\text{-}CH_2\text{-})_3(\mu\text{-}H)_2(CF_3CO_2)$ (**3**), was the main product of the reaction of trifluoroacetic acid with the μ_3-imidoyl complexes but a small amount of a monoprotonated species was observed to be in equilibrium with the adduct eq. (6). In the case of non-coordinating anions such as BF_4^-, only simple protonation was observed [6, 7].

We report here the results of studies on the coor-





dination chemistry of ammonia, aliphatic amines, and protic acids with **1,** in an attempt to define the stereodynamics of its coordination sites and how these differ from those observed in **2** and **3** (eqs. (5–6)). One of our research goals in developing the chemistry of complexes such as **1** was to understand the degree of electronic communication between the quinoline ring and the metal core. Our initial efforts in this area have resulted in the synthesis of the compounds $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}XC_9H_5N)(\mu\text{-}H)$ (X = 5-NH_2, **4**; 3-NH_2, **5**; 6-NH_2, **6**; 5-Br, **7**; 5-CH_3, **8**). We report here our initial results on the synthesis of these compounds according to the methods outlined in eqs. (1–4). Studies of their reactivity reveal the extraordinary impact of the electron deficient bonding mode of the cluster on the substituent in the 5-position and *vice versa*.

RESULTS AND DISCUSSION

Reactions with amines

The addition of a large excess (50 fold) of ammonia and various aliphatic amines to **1** results in an instant color change from green to orange and in the appearance of two new hydride peaks in the ^{1}H NMR in the range of -12 to -14 ppm (Table 1). The resonance at higher field (isomer I) is invariably in greater intensity (except in the case of NH_3) and the lower field resonance (isomer II) gradually increases in intensity until a final ratio (I/II), in the range of 0.5 to 4.8, is reached which does not change further (Table 1).

The ^{13}C NMR ($CDCl_3$, -60°C) of a ^{13}CO enriched sample of **1** treated with excess ammonia shows two sets of nine carbonyls (I: 187.3, 185.5, 185.6, 180.4, 179.8, 178.8 ($^2J^{13}C\text{-}^1H = 14$ Hz), 177.3($^2J^{13}C\text{-}^1H = 9$ Hz), 176.7, 176.2 ppm; II: 187.3, 186.7, 184.6, 182.0, 180.8, 177.8($^2J^{13}C\text{-}^1H = 12.5$ Hz), 177.5 ($^2J^{13}C\text{-}^1H = 9.6$ Hz), 176.8, 176.2 ppm). Significantly, the spectrum shows no resonances with ^{13}C satellites that, if present are indicative of a large *trans*-carbonyl coupling associated with the presence of an $Os(CO)_4$ group [5]. The previously reported amine complexes of triosmium clusters, **2** and **2′**, invariably have the amine (or ammonia) in an axial position eq. (5) [5]. Based on these facts alone, we can propose two alternative structures for the set of isomers formed from the interaction of amines with **1** eq. (7). One set has the hydride and the quinoline ring sharing a common edge while the amine occupies either axial site on the third, unbridged osmium atom (structures **A**, **A′**, eq. (7)). This structure is directly analogous to that observed related to μ_3 imidoyl complexes, **2** and **2′**, for which solid state structures are available eq. (5) [5].

On the other hand, coordination of the amine at the electron deficient osmium edge of **1** could lead to a structure where the quinoline ring and the hydride are on different edges with the amine occupying an axial position on the osmium atom bridged by the hydride but not by the quinoline ring structures **B**, **B′**, eq. (7)). This type of structure has been observed in the case of one imidoyl complex bearing ethyl and propyl groups on the imidoyl carbon and nitrogen atoms respectively eq. (8) [8]. We have also obtained indirect evidence for this structural type as a short-lived intermediate from the selective incorporation of

Table 1. Chemical Shifts (ppm) and Isomer Ratios for Amine Adducts of $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_9H_6N)(\mu\text{-}H)$, **1**.[1]

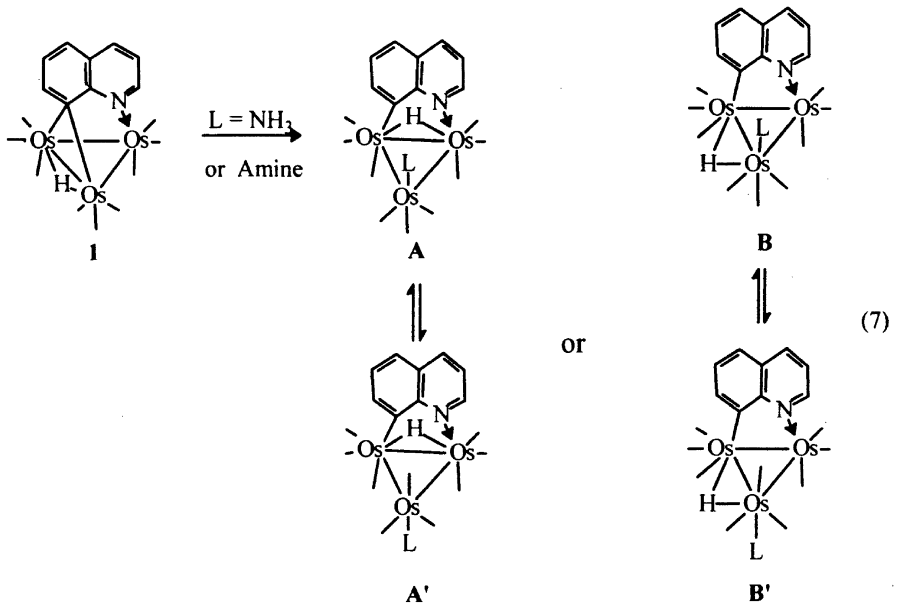
	Isomer 1	Isomer II	Solvent	Temperature	I/II
NH_3	−13.65 ppm	−13.05	$CDCl_3$	RT	0.5
	−13.40	−12.70	acetone	RT	1.3
$EtNH_2$	−13.66	−13.06	$CDCl_3$	RT	1.3
	−13.43	−12.77	acetone	−40°C	3.8
Et_2NH[a]	−13.80	—	$CDCl_3$	RT	—
t-$BuNH_2$	−14.12	−13.56	$CDCl_3$	−40°C	7.4
s-$BuNH_2$[b]	−13.59/	−12.97/	$CDCl_3$	−40°C	3.3
	−13.62	−13.00			
n-$BuNH_2$	−13.39	−12.76	$CDCl_3$	RT	2.8
$CyNH_2$	−13.61	−13.03	$CDCl_3$	RT	3.1
	−13.46	−12.81	acetone	RT	4.8

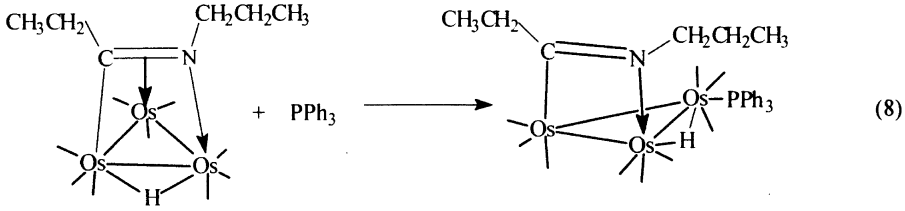
[a] only one isomer observed
[b] four hydride resonances observed

carbon monoxide into **1** [3]. In the case of phosphines reacting with **1**, such an intermediate is probably the initial product as well but goes on to rearrange as shown above eq. (2) [1, 3].

The initial formation of one isomer followed by the gradual appearance of a second has been shown to be an intermolecular process for the related μ_3-imidoyl complexes [5]. It would appear that this is also the case for **1** reacting with amines since the overall behavior of **1** towards amines is so similar [5]. The question of the structure of the amine adducts of **1** (**A** or **B**) still remains unanswered in the absence of a solid state structure.

The change in longitudinal relaxation time (T_1) of hydrides in metal clusters induced by proximal ligand protons can be used to qualitatively assess the distance between these two types of hydrogens [9]. Thus, for $Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}C_9H_6N)(\mu\text{-}H)$ (**9**) the T_1 of the hydride is 7.0 s while for **1** it is 4.0 s (Figure 1). We can attribute the shorter relaxation time in **1** to the proximity of the hydrogen of C(7) to the μ-hydride. If the amine adducts of **1** have a structure identical to their μ_3-imidoyl analogs then the T_1 of the μ-hydride would be expected to have a relaxation time similar to **9**. In fact, the T_1 of the ammonia adduct of **1** is 1.4 s which is consistent with a structure where the ammonia protons are proximal to the hydride; i.e., the structure resulting from addition of the ligand to the carbon bridged edge of the cluster without further rearrangement (structure **B**, eq. (7)).





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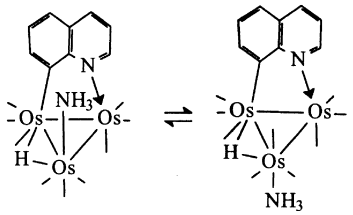
9 **1**

$T_1 = 7$ s $T_1 = 4$ s



B **B'**

$T_1 = 1.4$ s

Scheme 1.

This suggested structure is further supported by the ^{1}H NMR data obtained for the s-butyl adduct **1**. Here, four hydride resonances are observed. This is undoubtedly due to the presence of diastereomers induced by the presence of the chiral center on the s-butyl amine. In the structure proposed based on the T_1 measurements (structure B, eq. (7)), the environment on the osmium atom bound to the amine is quite asymmetric owing to the presence of the bridging hydride on one of the two edges of the triangle associated with the amine coordinated osmium atom. In the case of the structure adopted by the μ_3-imidoyl amine adducts (**2** and **2′** eq. (5)), the localized environment on the amine bound nitrogen is more symmetric and indeed only two hydride resonances are observed for the s-butyl complex [5].

Finally, the structure proposed is most consistent with a reversible amine coordination based on the principle of least motion since only the motion of the C(8) carbon pivoting on the coordinated nitrogen is required to reform **1** from its corresponding amine adduct. This motion is related to the reversible coordination of the C═N bond observed in the μ_3- to μ- to μ_3-imidoyl interconversions [5].

In our previous study of the imidoyl amine adducts, the initially formed isomer has the amine on the same face of the osmium triangle as the pyrrolidine ring (i.e., *syn*-) [5]. This isomer is more favored for the bulkier amines and this also appears to be the trend for the amine complexes of **1** Table 1. In fact, for the secondary amine Et_2NH only one isomer with a hydride chemical shift similar to the proposed *syn*-isomer is observed Table 1. Our initial thought for the imidoyl series was that the strictly sigma-bond framework of the pyrrolidine ring was less bulky than the carbonyl ligands which have π-electrons [5]. In light of the isomer ratios observed for the amine complexes of **1**, this cannot be the case since the quinoline ring also has π-electron density. Yet, the *syn*-isomer is still favored for bulkier ligands and the *anti*-isomer for the least bulky (ammonia). In order to further investigate this point, we measured the effect of temperature and solvent on the isomer ratio for three amine adducts of **1**. There are two obvious trends in the data (Table 2). First, it can be seen that the population of the *syn*-isomer is enhanced in the more polar solvent acetone Table 2. This, of course, is sensible in light of the expected greater polarity of the Os–

Table 2. ΔH° (kJ/mol) and ΔS° (J/mol K) for Amine Adducts of $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_9H_6N)(\mu\text{-}H)$, **1**[a2]

	k(I/II) 273 K	k(I/II) 298 K	ΔH° kJ/mol	ΔS° J/mol K	solvent
NH_3	0.52	0.49	-0.85 ± 0.19	-8.44 ± 0.77	$CDCl_3$
NH_3	1.55	1.33	-2.15 ± 0.75	-4.38 ± 2.9	Acetone
NH_2Et	1.22	1.34	3.35 ± 0.48	13.9 ± 1.8	$CDCl_3$
NH_2Et	4.0	3.85	2.20 ± 0.74	19.7 ± 2.9	Acetone
$CycNH_2$	3.45	3.07	-0.95 ± 0.54	6.76 ± 2.2	$CDCl_3$
$CycNH_2$	5.12	4.81 (extr.)	-1.44 ± 0.27	8.21 ± 1.1	Acetone

[a] Values and errors obtained by taking the least squares fit to the function $\ln I/II = \Delta H^\circ - T\Delta S^\circ$ for at least ten temperatures between 233 and 298 K.

N bonds with the quinoline and amine relative to the Os–CO bonds. Overall, the ΔH° values hover around zero, ranging from -3 to $+2$ kJ/mole. The most significant differences between compounds and between solvents are in the ΔS° Table 2. Significantly, the ammonia complex is the only one with a negative ΔS°. This indicates that solvation, not steric effects, can account for the observed differences in the isomer ratios. Apparently, the more polar *syn*- isomers lead to more disordered solute–solvent interactions and this effect is enhanced by the presence of non-polar substituents on the amine. That the larger cyclohexyl group shows a less positive ΔS° than the ethyl group is difficult to rationalize but may relate to the mobility of this ligand in the adduct.

The trends in the equilibrium constants for the formation of amine complexes with **1** follow the trends observed for the related μ_3 imidoyl species, *n*-Bu > *s*-Bu > *t*-Bu. The absolute values for the equilibrium constants for **1** however, are much greater being 44.4, 2.7, and 0.39; and 1.25, 0.37, and 0.005 for **1** and the μ_3-imidoyls respectively [5]. This undoubtedly reflects the greater electron deficiency for the $46e^-$ cluster relative to the reactive but electron-precise μ_3-imidoyls.

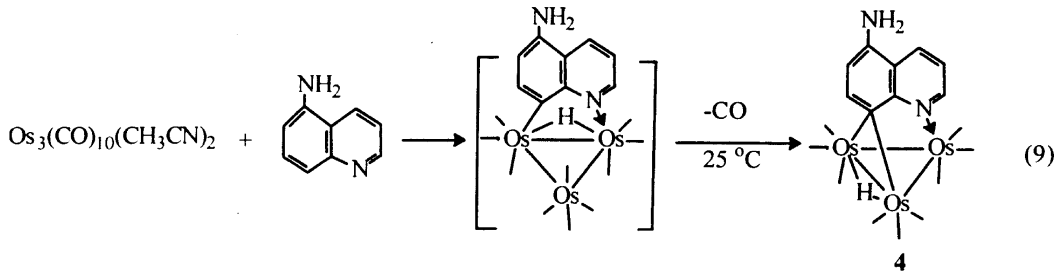
In order to assess the impact of an electron donating group on the coordination chemistry observed for **1**, we undertook the synthesis of the 3-, 5- and 6-amino analogs of **1**. The synthesis of these complexes proceeded in a straightforward manner. Significantly, the 5-amino derivative, $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}5\text{-}NH_2C_9H_5)(\mu\text{-}H)$ (**4**) formed directly, at ambient temperatures, without requiring thermal or photochemical decarbonylation eq. (9) [1–3]. This undoubtedly reflects the impact of the strong π-electron donor in a position *para*- to the incipient three center, two electron band. The 3- and 6-amino derivatives **5** and **6** did require the usual decarbonylation procedure (eqs. (10–11)). In all of these reactions (eqs. (9–11)) no detectable competition for coordination of the quinoline nitrogen by the aniline amino groups is seen but the yields of **5** and **6** were significantly lower than for **4** and **1**.

The reaction of **4** with *n*-$BuNH_2$ in both CD_2Cl_2 and CD_3OD showed no sign of complex formation even in the presence of a 100-fold excess of *n*-$BuNH_2$. This can be attributed to the electron donating ability of the amino group which funnels electron density down to the electron deficient C(8)–Os_2 bonding framework by conventional benzenoid resonance.

The 3- and 6-amino derivatives **5** and **6** do coordinate *n*-$BuNH_2$, as **1**. The formation constants are of the same order of magnitude as for **1**, with **6** showing a significantly larger formation constant than **5** or **1** (Table 3). As for **1**, isomer I, presumably the more polar isomer is favored with the equilibrium ratios of I/II being two to three times larger than for **1** Table 3. One might have expected the K_f for **6** to be less than that of **5** since the electron donating amino group is on the carbocyclic ring, albeit in the meta position. Clearly, the magnitude of K_f and the I/II ratio depend on a subtle combination of factors which cannot be delineated at this time. The one firm conclusion that can be drawn from these studies is the profound influence that substitution at the 5-position of the quinoline ring has on the electron density at the metal core. This is born out by our studies of the $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}(5\text{-}Br)C_9H_5N)(\mu\text{-}H)$ [4] (**7**) where the electron withdrawing bromine in the 5-position gives the largest K_f of all the derivatives of **1** investigated so far. In the case of $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}(5\text{-}CH_3)C_9H_5N)(\mu\text{-}H)$ [4] (**8**), where there is only a weakly electron donating group in the 5-position amine complex formation was also not observed even in the presence of a large excess of n-$BuNH_2$.

Reactions with protic acids

In order to further probe the electron distribution in **1** and **4**–**8** we investigated their reactions with CF_3CO_2H and HBF_4. Addition of a six-fold excess of CF_3CO_2H to a CD_2Cl_2 solution of **1** results in complete conversion to a deep orange solution which exhibits two hydride resonances at -13.66 and -11.61 ppm in a 1:1 ratio. The aromatic resonances are all shifted downfield with respect to **1**. An equilibrium constant for protonation was calculated from a titration of **1** with CF_3CO_2H (Table 4). The ^{13}C-



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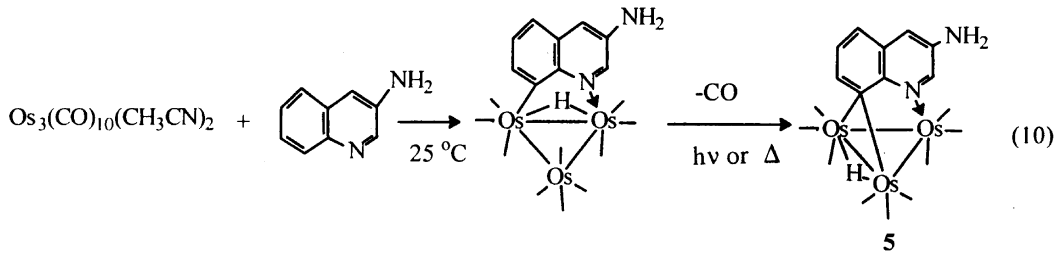

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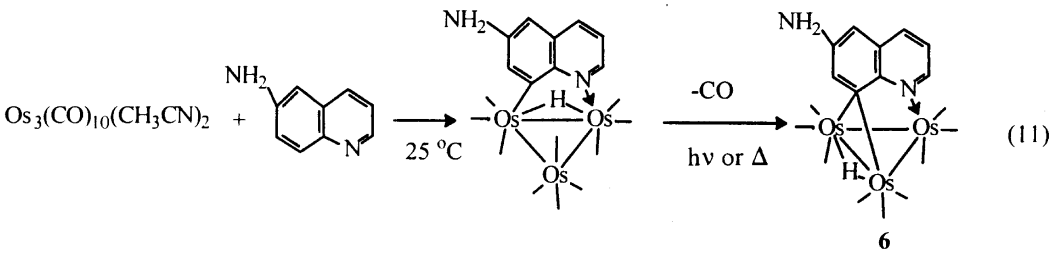

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Table 3. Equilibrium Constants and Isomer Ratios for n-BuNH$_2$ Complexes of Electron Deficient Quinoline Clusters[a3]

Compound	K_{FORM}	I/II	δ hydride I(II)	Solvent
1	44.4	2.8	−13.39(−12.76)	$CDCl_3$
5	53.9	7.3	−13.42(−12.81)	CD_2Cl_2
6	66.7	4.6	−13.42(−12.79)	CD_2Cl_2
7	94.5	1.2	−13.47(−12.90)	$CDCl_3$

[a] ±10% at 22°C

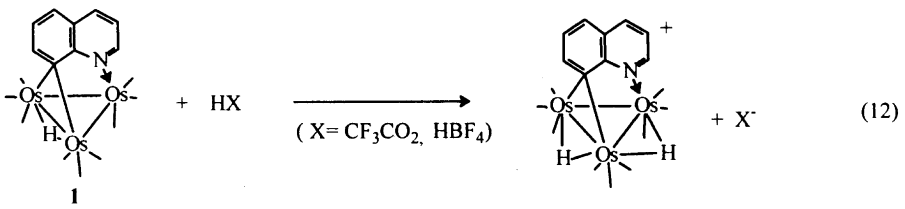
NMR (CD_2Cl_2) of a ^{13}CO sample of **1** in the presence of the same excess gives a ^{13}C NMR in the carbonyl region showing nine resonances at 180.65, 175.20, 172.50, 172.45, 171.01, 167.93, 166.52, 159.84, and 159.99 ppm. The two resonances at 159.84 and 158.99 ppm appear as doublets of doublets in the proton coupled spectrum ($^2J^{13}C$-$^1H = 13.74$, 4.58 and 13.73, 6.10 Hz respectively) while the two at 180.65 and 172.45 ppm appear as doublets ($^2J^{13}C$-$^1H = 9.15$ and 7.63 Hz). Protonation with the non-coordinating acid, HBF_4 yields the virtually identical ^1H Table 4 and ^{13}C NMR (CD_2Cl_2) data (180.61, 175.78, 172.92, 172.36, 171.43, 168.13, 166.71, 159.94, 158.85 ppm with an identical coupling pattern). These data are consistent with simple protonation to give a dihydride cation eq. (12) as opposed to acid adduct formation

Table 4. Protonation Equilibria for Electron Deficient Quinoline Triosmium Clusters[a4]

Compound	K_{eq}	Acid	δ hydrides	Solvent
1	0.12	CF_3CO_2H	−13.66 −11.61	$CDCl_3$
1	12.2	HBF_4	−13.70 −11.65	$CDCl_3$
4	20.8	CF_3CO_2H	−14.35 −12.60	$CDCl_3$
5	0.72	CF_3CO_2H	−13.81 −11.73	$CDCl_3$
6	1.88	CF_3CO_2H	−13.72 −11.70	$CDCl_3$
7	0.05	CF_3CO_2H	−13.78 −11.50	$CDCl_3$
8	1.19	CF_3CO_2H	−14.00 −12.15	$CDCl_3$

[a] Measured by ^1H NMR ±10% at +22°C

eq. (6). The equilibrium constant for formation of the cation is considerably larger for the stronger acid, HBF_4 Table 4. The observation of well resolved carbonyl–hydride couplings indicates that the protonated species is rigid on the NMR time scale while the hydrides in the related cationic μ_3-imidoyl species are fluxional at ambient temperatures.



(12)

The protonation of **4** with aliquots of CF_3CO_2H reveals that the 5-amino derivative is considerably more basic at the metal core than **1** Table 4. After the first aliquot (slightly in excess of 1 equivalent) is added, **4** is completely converted to the dihydride cation and the resonance at 5.60 ppm attributable to the amino resonance is no longer observed. Instead, a broad resonance at 7.82 ppm is observed which is attributable to a partially averaged signal of the CF_3CO_2H and the amino group of **4**. The CF_3CO_2H proton resonance is observed at 8.00 ppm in the presence of **1**. As more CF_3CO_2H is added to the solution of **4**, the acid amine resonance shifts to lower fields and sharpens somewhat indicating more rapid exchange between the amine and the acid. Significantly, the amine resonances for **5** and **6** are found at considerably higher fields than for **4** at 4.14 and 4.79 ppm respectively. On treatment with CF_3CO_2H, the same overall behavior as for **4** is observed for **5** and **6** except that the partially averaged acid/amine resonance is found between **5** and **6** ppm, suggesting a higher degree of amine protonation. The protonation equilibrium values (Table 4) obtained from these experiments are consistent with **4** having the greatest influence on the electron density at the metal core. A Hammett plot of the equilibrium data using standard values of σ[10] yields a reasonably good straight line with a correlation coefficient of 0.93 and ρ value of −0.13 (Figure 1).

CONCLUSIONS

The electron deficient μ_3-η^2-quinoline triosmium clusters exhibit behavior towards amines similar to the related μ_3-η^2 pyrrolidine triosmium clusters [5]. Both show initial formation of a single isomer which then equilibrates to a mixture of two complexes. The equilibrium constants in both series depend on the steric bulk of the amine with the overall magnitudes being much greater for the quinoline series. Based on the NMR evidence accumulated to date, the actual structure of the amine–quinoline adducts is different from that of the imidoyls. However, definitive conclusions about the actual structures must await solid

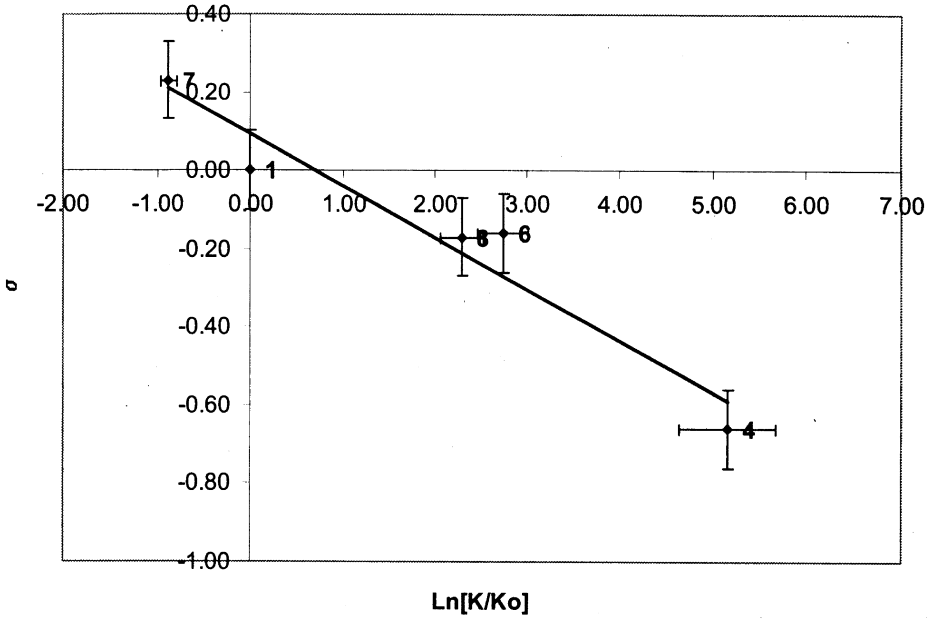


Fig. 1. Hammett, σ/ρ Plot of the Protonation Equilibria for Compounds **1**, **4**–**8** reacting with CF_3CO_2H (error bars for the σ values are from reference [10] and are $\pm 10\%$ for the K_{eq} values).

state structural determinations which have been difficult to obtain owing to the instability of the adducts as crystalline solids.

In sharp contrast to the μ_3-η^2-imidoyl clusters, the μ_3-η^2-quinoline clusters do not form acid adducts but simply undergo protonation in the presence of CF_3CO_2H.

The most interesting aspect of these studies is the profound influence that substituents in the 5-position have on the electronic properties of the metal core. That the simple free energy relationship normally applied to organic reactions can be used to rationalize the relationship between substitution on the carbocyclic ring and protonation at the metal core is reassuring in that it says that the relatively complex interactions (from an orbital point of view) between an organic moiety and two metal atoms can be understood in terms of a traditional physical organic chemistry model. The isomer I and II populations and the somewhat higher value of K_f for the 6-amino quinoline derivative, are less well understood, but seem to be dominated by solvation effects, at least from the data gathered so far.

EXPERIMENTAL

General: Compounds **1** [1], **7** [11] **8** [4], and 5-amino quinoline [11] and 5-bromo quinoline [11] were synthesized by known literature procedures. 3-Amino quinoline and 6-amino quinoline were purchased from Aldrich Chemical Co. and used as received. Methylene chloride was distilled from calcium hydride before use. Acetone-d_6, methylene chloride-d_2, and methanol-d_4 were purchased from Aldrich in single sample ampules and used as received. Chloroform-d_1 was dried over molecular sieves before use. NMR spectra were recorded on Jeol EX-400 or Varian Unity Plus 400 NMR spectrometers. Samples for T_1 measurement were previously degassed by three freeze thaw cycles. The non selective inversion recovery pulse sequence was used to obtain T_1 values. Infrared spectra were recorded on a Perkin–Elmer 1600 spectrometer and elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, New York.

Preparation of $Os_3(CO)_9(\mu_3$-η^2-(5-NH_2)$C_9H_5N)(\mu$-$H)$ ***4***. $Os_3(CO)_{10}(MeCN)_2$ (0.250 g, 0.268 mmol) was dissolved in CH_2Cl_2 (150 mL) and 5-amino quinoline (0.080 g, 0.5 mmol) was added. The reaction mixture was stirred for 16 h at room temperature. The resulting deep green solution was separated and filtered through a 14″ silica gel column eluted with hexane/CH_2Cl_2 (70:30), giving two bands. The first yellow band was a mixture of the isomers $Os_3(CO)_{10}(\mu$-η^2-(5-NH_2)$C_9H_5N)(\mu$-H) (less than 10%). The second fraction yielded (0.223 g, 0.219 mmol, 82.1% overall from $Os_3(CO)_{10}(CH_3CN)_2$) of the green major product, **4**, $Os_3(CO)_9(\mu_3$-η^2-(5-NH_2)$C_9H_5N)(\mu$-H) which gave green crystals from hexane/CH_2Cl_2 at -20C.

Analytical and spectroscopic data for $[Os_3(CO)_9(\mu_3$-η^2-(5-NH_2)$C_9H_5N)(\mu$-$H)]$ ***4***. Anal. calcd for $C_{18}H_8N_2O_9Os_3$: C, 22.38, H, 0.78; N, 2.76. Found: C, 22.37; H, 0.75; N, 2.83. IR (ν(CO) in hexane): 2080w, 2069m, 2040s, 2013s, 1981s, 1967w cm^{-1}. ^{1}H-NMR at 400 MHz in $CDCl_3$: δ 9.25 (dd, H(2)), 7.07 (t, H(3)), 8.00 (dd, H(4)), 8.16 (dd, H(6), 6.43 (d, H(7)), 5.60 (broad singlet, NH_2), -13.01 (s, hydride).

Synthesis of $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}(n\text{-}X)C_9H_5N)(\mu\text{-}H)$, ***5*** (n = 3, $X = NH_2$), ***6*** (n = 6, $X = NH_2$), ***7*** (n = 5, $X = Br$). $Os_3(CO)_{10}(CH_3CN)_2$ (0.250–0.500 g, 0.27–0.54 mmol) was dissolved in 150–200 mL CH_2Cl_2 and a two-fold molar excess of the substituted quinoline was added by syringe. The solution was stirred for 16–20 h and then filtered through a small silica gel column to remove excess ligand and a small amount of brown decomposition product. The yellow methylene chloride solution was then photolyzed using a Rayonet photochemical reaction chamber equipped with 300 nm lamps for 2–4 h or until the infrared spectrum showed essentially complete conversion to the green nonacarbonyl derivative. The green methylene solution was then concentrated and purified by thin layer chromatography using 1:1 hexane/methylene chloride (for **5** and **6**) or 7:3 hexane/methylene chloride (for **7**). Yields for **5** and **6** ranged from 50–60% while those for **7** were 80–85%.

Analytical and spectroscopic data for $Os_3(CO)_9(\mu_3\text{-}\eta^2(3\text{-}NH_2)C_9H_5N)(\mu\text{-}H)$ ***5***. Calculated for $C_{18}H_8N_2O_9Os_3$: C, 22.38; H, 0.78; N, 2.76. Found: C, 22.12; H, 1.02; N, 2.84. IR(ν(CO) in CH_2Cl_2): 2076w, 2050s, 2017s, 1989m, br cm^{-1}. ^1H NMR at 400 MHz in Acetone-d_6: δ 9.31(d, 1H), 8.68(dd, 1H), 8.61(dd, 1H), 7.41(d, 1H), 7.30(dd, 1H), 4.14(s, br, 2H), −12.23(s, 1H).

Analytical and spectroscopic data for $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}(6\text{-}NH_2)C_9H_5N)(\mu\text{-}H)$ ***6***. Calculated for $C_{18}H_8N_2O_9Os_3$: C, 22.38; H, 0.78; N, 2.76. Found: C, 22.49, H, 0.86; N, 2.71. IR (ν(CO) in CH_2Cl_2): 2076w, 2041s, 2018s, 1988m, br, 1973w, br cm^{-1}. ^1H NMR at 400 MHz in $CDCl_3$: δ 8.92(dd, 1H), 7.83(d, 1H), 7.79(dd, 1H), 7.36(d, 1H), 6.97(dd, 1H), 4.79(s, br 2H), −12.23(s, 1H).

Spectroscopic and analytical data for $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}(5\text{-}Br)C_9H_5N)$ ***7***. Calculated for $C_{18}H_6NO_9BrOs_3$: C, 20.97; H, 0.48, N, 1.36. Found: C, 20.84; H, 0.38; N, 1.37; IR(ν(CO) in CH_2Cl_2): 2077m, 2050s, 2020s, 1990s, 1977w, 1952w cm^{-1}. ^1H NMR at 400 MHz in $CDCl_3$: δ 9.32(dd, 1H), 8.49(dd, 1H), 8.39(d, 1H), 7.46(d, 1H), 7.19(dd, 1H), −12.07(s, 1H).

Evaluation of isomer ratios and equilibrium constants. Compounds **1** or **4**–**8**, were weighed directly into flame dried NMR tubes in 9–11 mg samples (~0.01 mmol). 0.60 mL of the NMR solvent was then added by syringe, followed by syringe addition of 2–20 μL of the amine or acid. The NMR tube was then capped and shaken and the proton or ^{13}C NMR monitored for at least 24 h after which time no further changes in the spectra were observed. The isomer ratios and equilibrium constants were evaluated by integration of the appropriate resonances. For formation constants, the equilibrium expression was:

$$K_f(\mathrm{L/mol}) = \frac{[\mathrm{cluster-amine\ adduct}]}{[\mathrm{cluster}][\mathrm{amine}]}$$

in most cases the equilibrium constant was evaluated at several concentrations of added amine and an average value is reported in Table 3. For the protonation equilibrium, the expression used was:

$$K_p = \frac{[\mathrm{clusterH^+}][\mathrm{X^-}]}{[\mathrm{cluster}][\mathrm{HX}]}$$

Again, the value of the equilibrium constant was evaluated at several acid concentrations in most cases.

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