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QUINOLINE BINDING MODE AS A FUNCTION OF OXIDATION STATE IN ARYLOXIDE-SUPPORTED TANTALUM COMPLEXES: MODELS FOR HYDRODENITROGENATION CATALYSIS

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Abstract—The heterocyclic complexes $[\eta^1(N)$-QUIN]$Ta(OAr)_3Cl_2$ (**1**) and $[\eta^1(N)$-6MQ]$Ta(OAr)_3Cl_2$ (**2**) (where Ar = 2,6-diisopropylphenyl, QUIN = quinoline, and 6MQ = 6-methylquinoline) are prepared from $Ta(OAr)_3Cl_2(OEt_2)$ and QUIN or 6MQ in pentane. $[\eta^1(N)$-6MQ]$Ta(OAr)_2Cl_3$ (**4**) is prepared similarly from $Ta(OAr)_2Cl_3(OEt_2)$. Upon rapid, two-electron reduction of these complexes, an $\eta^1(N) \rightarrow \eta^2(N,C)$ bonding rearrangement is effected and the thermally sensitive, d^2 species $[\eta^2(N,C)$-QUIN]$Ta(OAr)_3$ (**5**), $[\eta^2(N,C)$-6MQ]$Ta(OAr)_3$ (**6**), and $[\eta^2(N,C)$-6MQ]$Ta(OAr)_2Cl(OEt_2)$ (**9**) can be isolated. Alternatively, $[\eta^2(N,C)$-6MQ]$Ta(OAr)_2Cl(OEt_2)$ (**9**) can be prepared in higher yield from $(\eta^6$-$C_6Me_6)Ta(OAr)_2Cl$ and 6MQ. The trimethylphosphine adducts $[\eta^2(N,C)$-QUIN]$Ta(OAr)_3(PMe_3)$ (**7**) and $[\eta^2(N,C)$-6MQ]$Ta(OAr)_3(PMe_3)$ (**8**) can be prepared by simple coordination of PMe_3 to the base-free compounds **5** and **6**. When $Ta(OAr)_2Cl_3(OEt_2)$ is reduced by one electron in the presence of QUIN, 6MQ, or pyridine, the d^1 bis(ligand) complexes $[\eta^1(N)$-QUIN]$_2Ta(OAr)_2Cl_2$ (**10**), $[\eta^1(N)$-6MQ]$_2Ta(OAr)_2Cl_2$ (**11**), and $[\eta^1(N)$-py]$_2Ta(OAr)_2Cl_2$ (**12**) can be isolated. Complexes **10** and **11** are not readily converted to the $\eta^2(N,C)$ analogues **5** and **6** by further reduction. Under mild hydrogenation conditions, the only heterocyclic ligands which are hydrogenated are those bound in the $\eta^2(N,C)$ mode to a d^2 metal. Structural studies on $[\eta^2(N,C)$-6MQ]$Ta(OAr)_3(PMe_3)$ (**8**) and $[\eta^2(N,C)$-6MQ]$Ta(OAr)_2Cl(OEt_2)$ (**9**) have been undertaken. $[\eta^2(N,C)$-6MQ]$Ta(OAr)_3(PMe_3)$ (**8**) crystallizes in the monoclinic space group $C2_1/c$ (No. 15) with $a = 32.849$ (3) Å, $b = 19.579$ (2) Å, $c = 23.822$ (2) Å, $\beta = 135.69$ (49)°, and $V = 10702$ (2) Å^3 with $Z = 8$ and $\rho_{calcd} = 1.16$ g cm^{-3}. $[\eta^2(N,C)$-6MQ]$Ta(OAr)_2Cl(OEt_2)$ (**9**) crystallizes in the monoclinic space group $P2_1/n$ (No. 14) with $a = 12.059$ (9) Å, $b = 17.975$ (14) Å, $c = 17.949$ (13) Å, $\beta = 100.29$ (3)°, and $V = 3828$ (9) Å^3 with $Z = 4$ and $\rho_{calcd} = 1.37$ g cm^{-3}. Both structures indicate an interruption of aromaticity to the heterocyclic ring only when bound in this fashion, consistent with the observation of 1,2,3,4-tetrahydroquinoline as the principal hydrogenation product of $[\eta^2(N,C)$-QUIN]$Ta(OAr)_3$ (**5**) with no decahydroquinoline being observed.

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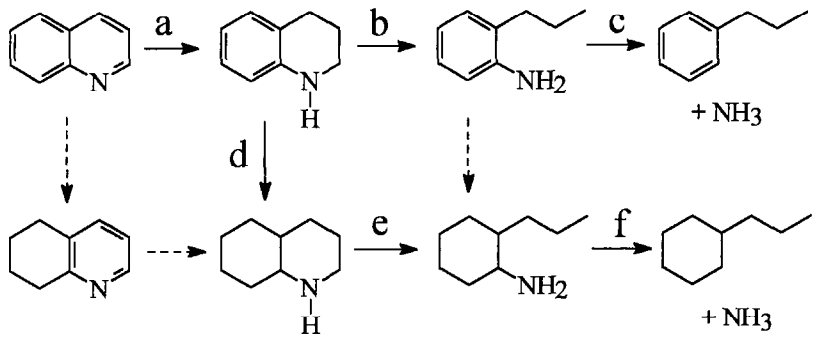


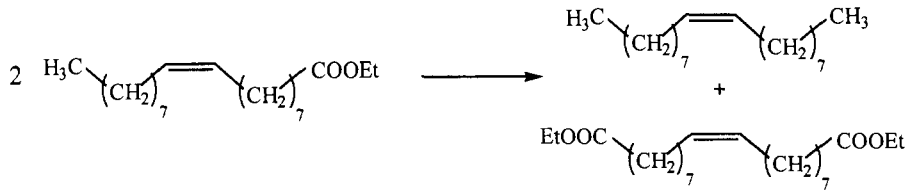
Scheme 1.

Hydrodenitrogenation (HDN) is the process by which organic nitrogen is removed from petroleum and coal derived liquids to provide more processable and environmentally sound liquid fuel stocks.[1-7] Performing HDN is essential to reduce the emissions of NO_x upon burning these fuels and because nitrogen-containing compounds significantly reduce the activity of hydrocracking and hydrotreating catalysts. Industrial HDN catalysis is generally effected over sulphided CoMo/γ-Al_2O_3 or NiMo/γ-Al_2O_3 under rather severe hydrogenation conditions (e.g. 350–500°C and $\geqslant$2000 psi H_2), which ultimately removes the nitrogen as NH_3.[1,2,8,9] The most active site for HDN reactions in the sulphided CoMo catalyst appears to be crystallites of MoS_2 supported on γ-alumina, with Co atoms adsorbed along the edges of the MoS_2 layered structure.[8] An Mo—S site of this "CoMoS" phase is usually associated with nitrogen heterocycle activation while hydrogen is usually described as dissociatively bound to sulphur in the form of sulphhydryl groups.[1,2,8] Evidence has been presented that suggests an electron transfer role for cobalt in HDN reactions.[10] Several non-molybdenum catalysts have also been used in HDN such as vanadium,[1] niobium sulphides,[11] ruthenium sulphide,[12] both NiW/Al_2O_3 and NiW/zeolite phases,[1] as well as other supports such as zirconia.[13]

Both heterocyclic (containing pyridine or pyrrole rings) and non-heterocyclic (aliphatic amines and anilines) nitrogen-containing compounds are found as contaminants in petroleum and are subject to HDN catalysis.[5] By far the most difficult nitrogen contaminants to process are the heterocyclic compounds. Because of the complexity of studying crude oil, the HDN reactions of model compounds have been examined; quinoline is a prototypical HDN substrate which has proved particularly valuable in model studies.[4-7,14] While it is difficult to make generalizations from one set of catalyst and conditions to another, the collective evidence points to the quinoline HDN reaction network shown in Scheme 1.[4,14-20] Clearly, the most efficient and selective pathway involves the reactions a → b → c in which the non-heteroatom ring is *not* hydrogenated. This path represents a considerable saving in hydrogen and provides a higher quality (higher octane) product.[4] However, *most* of the quinoline which undergoes HDN is hydrogenated along the a → d → e → f pathway, where the non-heteroatom ring is also hydrogenated before C—N bonds are cleaved.[21] (Kinetic studies suggest that the dashed lines are not primary hydrogenation/hydrogenolysis pathways for quinoline.[15-17,22,23])

Only a handful of studies have attempted to correlate heterocycle hydrogenation with substrate–metal binding interactions,[7,15-17,24-29] yet these must be intimately related since the preferred substrate binding mode is expected to dictate the extent and selectivity of ring hydrogenation. Figure 1 depicts possible pyridine and quinoline bonding modes, all of which have been discussed with respect to HDN and many of which are known in isolable complexes. Observed bonding modes of pyridine (and its derivatives) include the $\eta^1(N)$,[30] the $\eta^6(\pi\text{-}N)$,[31] and the recently discovered $\eta^2(N,C)$[32,33] and $\eta^2(C,C)$[34] structures, as well as the very rare $\mu\text{-}\eta^1(N)$[35] mode. Furthermore, when considering the bonding modes of polyaromatic compounds such as quinoline, the $\eta^6(\pi\text{-}C)$[36] and an $\eta^2(C,C)$ mode involving the benzene ring become possible, though only the $\eta^1(N)$,[30,36] $\eta^6(\pi\text{-}C)$,[36] and $\eta^2(N,C)$[33] modes have been described (Fig. 1).

The η^1-(N)- and $\eta^6(\pi\text{-}N)$-bound heterocyclic compounds are the most often discussed with respect to interactions of the active site of the heterogeneous CoMoS catalyst.[1,37,38] Most *homogeneous* studies have also centred around these bonding modes. For example, both the binding modes and hydrogenation behaviour of heteroaromatic compounds have been examined by Fish and co-workers using soluble rhodium- and ruthenium-cyclopentadienyl complexes.[24-27,36,39] In these species, heterocycle $\eta^1(N)$ bonding appears to



Scheme 6.

$(O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_3$ exhibited a very particular behaviour, easily applied for RIM technology: there was an induction priod of a few minutes which was followed by a very fast polymerization. The induction period depended on two parameters:

(i) the Al/W ratio; below an Al/W ratio of 6, the reaction proceeded very slowly, whereas above this value the induction period decreased until a limiting value of *ca* 10 min (for a length of interaction of 10 min);

(ii) the length of interaction between the catalyst and the cocatalyst before introduction of the dicyclopentadiene: the greater the length of interaction, the longer the induction period.

When the aryloxide was the *p*-methoxyphenol, it was proposed that the induction period was due to a competitive coordination of the *p*-methoxy group of one aryloxide and the dicyclopentadiene. In the case of the 2,6-di-isopropyl phenoxide, it was explained by a competition between the coordination of the dicyclopentadiene and an intramolecular C—H activation of a methyl group of one ligand.

When the polymerization was carried out with alkyl-tin or alkyl-lead as cocatalysts, the reaction proceeded more slowly and no solidification of the reaction mixture was observed. The polymerization depended on the cocatalyst and decreased in the order $PbBu_4 > SnBu_4 > SnMe_4$. Analysis of the polymer showed that it was linear with a low degree of cross-linking (as depicted in Scheme 3).

The ring-opening metathesis polymerization of dicyclopentadiene demonstrates the wide versatility of the chloro-aryloxide complexes of tungsten as olefin metathesis catalysts. Indeed, depending on the cocatalyst, a highly cross-linked insoluble or a linear soluble material can be obtained, the rate of polymerization being controlled by the nature of the aryloxide ligands and of the cocatalyst. Finally, some catalysts compatible with the RIM processes (very fast polymerization after an induction period) were obtained.

METATHESIS OF OLEFINIC ESTERS WITH $W(OAr)_xCl_{6-x}+MR_4$ (M = Sn, Pb; R = Me, Bu) AND WITH $W(OAr)(OAr)(=CHC(CH_3)_3)(OEt_2)Cl$ (OAr = O-2,6-$C_6H_3Ph_2$ OR O-2,6-$C_6H_3Cl_2$)

One of the challenges of organic chemistry is the metathesis of functional olefins. For example, this can lead to a simple one-step synthesis of difunctional olefins, useful starting materials which are sometimes difficult to obtain by the classical methods of organic chemistry. What has now virtually become a test of the tolerance of metathesis catalysts towards functional groups is the metathesis of an olefin bearing an ester group such as ethyl oleate (ethyl-9-octadecenoate) (Scheme 6).

The bis-aryloxide precursors $W(O\text{-}2,6\text{-}C_6H_3X_2)_2Cl_4$ (X = Cl, Br), when associated with homoleptic alkyl-tin or alkyl-lead derivatives, achieve metathesis of ethyl oleate with good activities and selectivities and rather high substrate/catalyst ratios. In most cases, the results are better than those reported for the conventional homogeneous catalyst WCl_6/SnR_4: for example, metathesis of ethyl oleate by the system $W(O\text{-}2,6\text{-}C_6H_3Cl_2)Cl_4/PbBu_4$ (reaction conditions: solvent C_6H_5Cl, temperature 85°C, $[W] = 10^{-4}$ mol, Pb/W = 2, substrate/catalyst = 50, catalyst–cocatalyst interaction time: 20 min) leads to 50% conversion after 30 min, with a 28% yield in the corresponding diester.[6] The chloro-aryloxide catalysts also appear particularly interesting for the cometathesis of unsaturated esters with olefins, since the selectivity in cross-metathesis can reach 90%.

As expected, much better results were obtained with **1**, as approximately 50% of 500 equivalents of ethyl oleate was selectively converted to 9-octadecene and diethyl-9-octadecenedioate, in 60 min at 25°C. The initial turnover rate for the conversion of ethyl oleate is higher than 800 h^{-1} (Fig. 4), a value which is, to our knowledge, one of the highest activities reported for the metathesis of that substrate[22] and the highest with a tungsten-based catalyst.[23,24]

these compounds are entirely consistent with the simple $\eta^1(N)$ mode of heterocycle bonding to the d^0 metal. In particular, the resonances attributed to the H(2) and H(8) protons of the quinoline ligand in $[\eta^1(N)\text{-QUIN}]Ta(OAr)_3Cl_2$ (**1**) are shifted downfield with respect to those of the free ligand in the ^1H NMR (toluene-d_8, 373 K, Table 1). This shift appears to be a manifestation of these protons' proximity to the electrophilic d^0 metal centre when the heterocycle is coordinated in this fashion.[43] A similar observation is made for $[\eta^1(N)\text{-6MQ}]Ta(OAr)_3Cl_2$ (**2**).

The room temperature ^1H NMR spectra of **1** and **2** are characterized by broad, featureless signals suggesting a fluxional process of the order of the NMR timescale. At elevated temperatures, the ^1H NMR spectra (toluene-d_8, 373 K) of these complexes sharpen and become extremely simple, showing only the resonances attributed to the nitrogen heterocycle and only *one* type of aryloxide ligand. This equivalence of the OAr ligands at high temperatures most likely stems from two dynamic processes: (i) rapid dissociation of the heterocycle to establish the equilibrium $[\eta^1(N)\text{-QUIN}]Ta(OAr)_3Cl_2 \rightleftharpoons Ta(OAr)_3Cl_2 + QUIN$, and (ii) facile isomerization and equilibration of the OAr ligands of nascent, five-coordinate $Ta(OAr)_3Cl_2$.

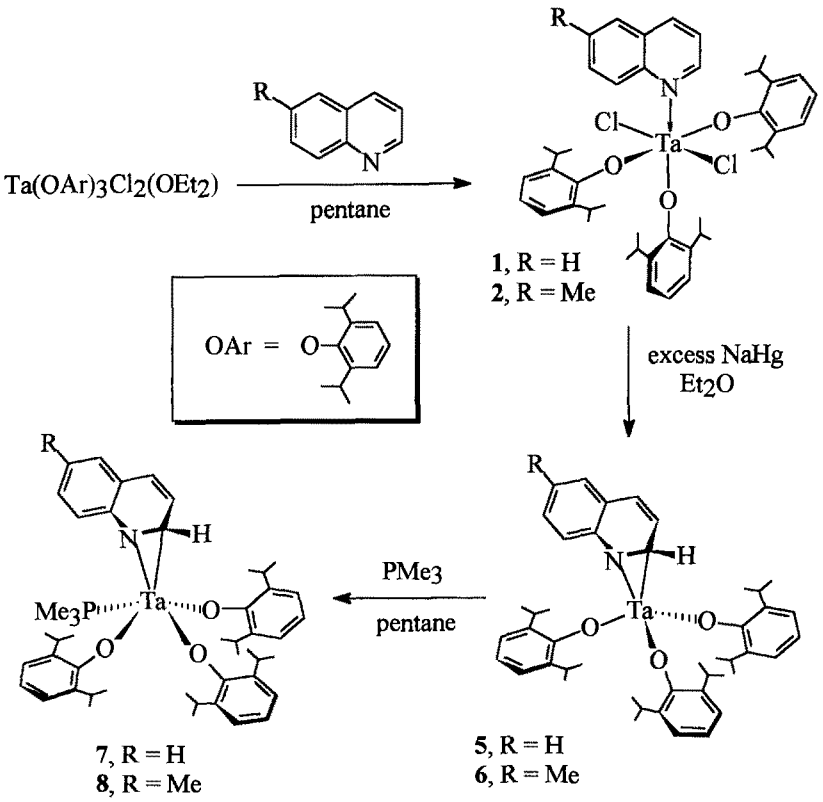
Table 1. Comparison of the ^1H and ^{13}C chemical shifts (in C_6D_6) for the α-CH group in $\eta^1(N)$- and $\eta^2(N,C)$-bound quinoline and 6-methylquinoline

Complex	δ ^1H	δ ^{13}C
$[\eta^1(N)\text{-QUIN}]Ta(OAr)_3Cl_2$ (**1**)	9.63 (9.50[a])	155.4[a]
$[\eta^1(N)\text{-6MQ}]Ta(OAr)_3Cl_2$ (**2**)	9.62 (9.24[a])	152.6[a]
$[\eta^1(N)\text{-6MQ}]Ta(OAr)_2Cl_3$ (**4**)	9.78	155.3
$[\eta^2(N,C)\text{-QUIN}]Ta(OAr)_3$ (**5**)	4.07	76.4
$[\eta^2(N,C)\text{-6MQ}]Ta(OAr)_3$ (**6**)	4.11	76.6
$[\eta^2(N,C)\text{-QUIN}]Ta(OAr)_3(PMe_3)$ (**7**)	3.62	67.5
$[\eta^2(N,C)\text{-6MQ}]Ta(OAr)_3(PMe_3)$ (**8**)	3.68	67.4
$[\eta^2(N,C)\text{-6MQ}]Ta(OAr)_2Cl(OEt_2)$ (**9**)	4.69	*b*

[a] Toluene-d_8 data.
[b] Not recorded.

This contention is supported by the reaction of $[\eta^1(N)\text{-QUIN}]Ta(OAr)_3Cl_2$ (**1**) with free 6-methylquinoline, which provides significant concentrations of $[\eta^1(N)\text{-6MQ}]Ta(OAr)_3Cl_2$ (**2**) as well as free quinoline (^1H NMR).

As a part of this study, we examined compounds with fewer steric constraints than those presented in the tris(aryloxide) compounds **1** and **2**; thus, the



Scheme 2.

reaction of N-heterocycles with the bis(aryloxide) complex $Ta(OAr)_2Cl_3(OEt_2)$ was examined. Pentane slurries of $Ta(OAr)_2Cl_3(OEt_2)$ react with quinoline to afford a bright yellow precipitate in high yield formulated as $[\eta^1(N)$-QUIN]Ta$(OAr)_2Cl_3$ (**3**). This complex is very insoluble in organic solvents with which it does not react, which has precluded its full spectroscopic characterization. For example, while $[\eta^1(N)$-QUIN]Ta$(OAr)_2Cl_3$ (**3**) dissolves in pyridine-d_5, the ^{1}H NMR spectrum of this solution reveals that quinoline has been displaced such that only unbound quinoline (1 equiv.) and presumably $[\eta^1(N)$-$NC_5D_5]Ta(OAr)_2Cl_3$ are present in solution.

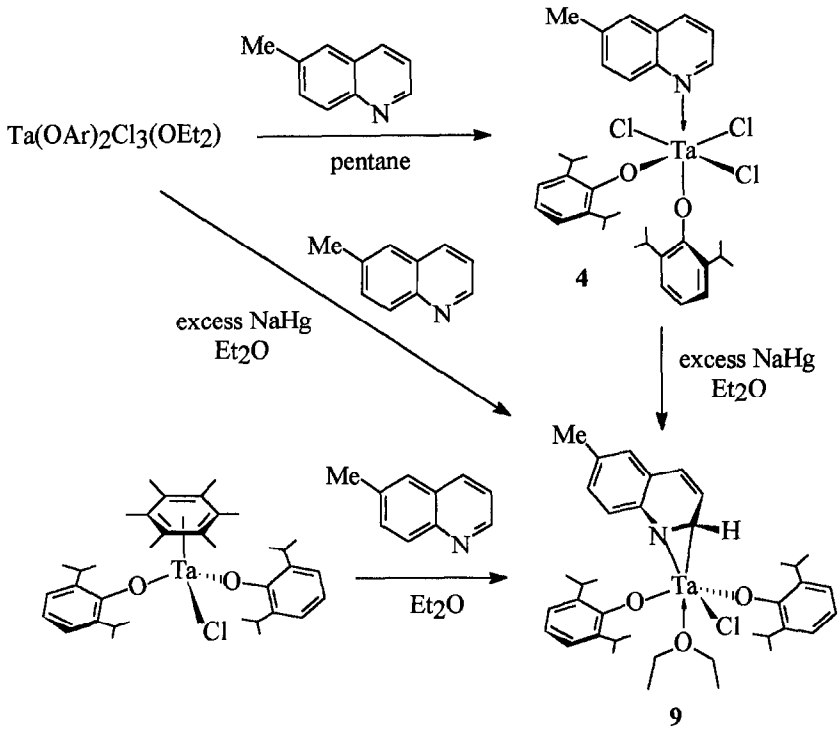
The 6-methylquinoline analogue of **3**, $[\eta^1(N)$-6MQ]Ta$(OAr)_2Cl_3$ (**4**), is isolated by a similar procedure and in equally high yields, though **4** is much more soluble than **3** (Scheme 3). The ^{1}H NMR resonances (C_6D_6, room temperature) assigned as H(2) and H(8) of the 6MQ ligand in **4** are also shifted downfield relative to the free ligand. However, unlike compounds **1** and **2**, the ^{1}H NMR spectrum of **4** is characterized by sharp signals at room temperature with the *i*-propyl groups of the OAr ligands exhibiting two C*H*Me$_2$ septets and two CH*Me*$_2$ doublets. This observation is consistent with a *cis,mer*-geometry in a static structure. The OAr ligands of $[\eta^1(N)$-6MQ]Ta$(OAr)_2Cl_3$ (**4**) become equivalent in the ^{1}H NMR upon heating, suggesting the rapid dissociation of the heterocycle to establish an equilibrium $[\eta^1(N)$-6MQ]Ta$(OAr)_2Cl_3 \rightleftharpoons Ta(OAr)_2Cl_3 + 6MQ$, along with the facile isomerization and equilibration of the OAr ligands of five-coordinate $Ta(OAr)_2Cl_3$. This suggestion appears especially plausible in view of the isolation of the base-free analogue of these compounds, $Ta(OAr)_2Cl_3$.[44] Finally, the 6-methylquinoline ligand in **4** is also readily displaced as is evidenced by its ^{1}H NMR spectrum in pyridine-d_5, which clearly shows all the 6-methylquinoline present in this sample is unbound.

Quinoline binding mode as a function of oxidation state: an $\eta^1(N) \rightarrow \eta^2(N,C)$ *transformation upon reduction*

When cold Et_2O solutions of $[\eta^1(N)$-QUIN]Ta$(OAr)_3Cl_2$ (**1**) are *rapidly* reduced in the presence of a large excess of NaHg, dark red solutions are obtained from which the *highly* soluble, thermally sensitive, burgundy compound **5** can be isolated (Scheme 2). Spectroscopic data (^{1}H and ^{13}C NMR) suggest the formulation $[\eta^2(N,C)$-QUIN]Ta$(OAr)_3$ for **5** in which the heterocycle has undergone an $\eta^1(N) \rightarrow \eta^2(N,C)$ bond mode rearrangement upon complex reduction (Table 1). Most significantly, the quinoline CαH resonance at δ 9.62 in the ^{1}H NMR spectrum of $[\eta^1(N)$-QUIN]Ta$(OAr)_3Cl_2$ (**1**) has shifted to δ 4.08 in $[\eta^2(N,C)$-QUIN]Ta$(OAr)_3$, diagnostic of $\eta^2(N,C)$ bonding and reflecting a rehybridization of C(2).[32] Because of its *extreme* solubility as well as its thermal sensitivity, **5** has not been obtained completely pure (*vide infra*). Rapid reduction of the 6-methylquinoline adduct **2** also effects a heterocycle $\eta^1(N) \rightarrow \eta^2(N,C)$ bonding rearrangement and $[\eta^2(N,C)$-6MQ]Ta$(OAr)_3$ (**6**) can be obtained in good yield. These complexes are spectroscopically similar to Wolczanski's complex $[\eta^2(N,C)$-$NC_5H_5]Ta(silox)_3$ (silox = OSi-*t*-Bu$_3$), which is prepared directly from d^2 Ta$(silox)_3$ and pyridine.

One particularly interesting aspect of the synthesis of $[\eta^2(N,C)$-QUIN]Ta$(OAr)_3$ (**5**) is the fact that the reduction reaction must be executed with "preformed" **1** in which the quinoline ligand is already coordinated; simply reducing Et_2O solutions of $Ta(OAr)_3Cl_2(OEt_2)$ in the presence of 1 equiv. of quinoline affords **5** in only insignificant yields. This observation can perhaps be attributed to, *inter alia*, the instability of **5** towards free quinoline, a feature which has precluded *catalytic* hydrogenation studies using this complex. Thus, the reaction of **5** with quinoline provides (after hydrolysis) significant quantities of 2,2′-biquinoline (by GC-MS). Because aqueous quenching of **5** alone provides free quinoline and HOAr as the *only* organic products (and *no* 2,2′-biquinoline), the formation of biquinoline is clearly a result of the reaction between **5** and quinoline and not an artifact of the work-up procedure. A further difficulty in studying complex **5** is its extreme thermal sensitivity. Solutions of $[\eta^2(N,C)$-QUIN]Ta$(OAr)_3$ (**5**) decompose quickly at room temperature in non-coordinating solvents (e.g. benzene) to provide dark solutions which, upon hydrolysis and Et_2O extraction, also afford 2,2′-biquinoline as the major (and only identifiable) nitrogen-containing product. This observation is significant since, under HDN reaction conditions using metal sulphide catalysts, dehydrogenation of tetrahydroquinoline has been reported to produce biquinolines.[45]

Because of the difficulty in isolating, purifying and manipulating compounds **5** and **6**, base adducts were prepared which proved to be much more thermally stable. Thus, reacting pentane solutions of **5** or **6** with excess PMe_3 affords orange crystals of the adducts $[\eta^2(N,C)$-QUIN]Ta$(OAr)_3(PMe)$ (**7**) and $[\eta^2(N,C)$-6MQ]Ta$(OAr)_3(PMe_3)$ (**8**) (Scheme 2). Both adducts proved to be considerably more stable—though less reactive—than their base-free analogues, which afforded an opportunity for a structural characterization of **8** (*vide infra*).



Scheme 3.

Reduction of the bis(aryloxide) complex $[\eta^1(N)$-6MQ]$Ta(OAr)_2Cl_3$ also induces a heterocycle $\eta^1(N) \rightarrow \eta^2(N,C)$ bonding rearrangement, though the resulting product is even *more* thermally sensitive than **5** and **6** described above. Thus, preparing $[\eta^1(N)$-6MQ]$Ta(OAr)_2Cl_3$ *in situ* from $Ta(OAr)_2Cl_3(OEt_2)$ and 6MQ (in cold Et_2O solution) and *rapidly* reducing with excess NaHg (3–4 equiv.) affords a moderate to low yield of a complex shown to be the etherate $[\eta^2(N,C)$-6MQ]$Ta(OAr)_2Cl(OEt_2)$ (**9**). No gains in yield can be made from using preformed $[\eta^1(N)$-6MQ]$Ta(OAr)_2Cl_3$ (**4**). Because $[\eta^2(N,C)$-6MQ]$Ta(OAr)_2Cl(OEt_2)$ (**9**) prepared by this route is invariably contaminated with a paramagnetic impurity that is virtually impossible to separate from **9** (*vide infra*), another approach to this species was developed. Thus, upon reacting the arene complex $(\eta^6\text{-}C_6Me_6)Ta(OAr)_2Cl$[41a] with 6-methylquinoline, $[\eta^2(N,C)$-6MQ]$Ta(OAr)_2Cl(OEt_2)$ and free C_6Me_6 are formed in virtually quantitative yield. All attempts to prepare the quinoline analogue of **9** have afforded intractable oils.

Structural study of $[\eta^2$(N,C)-6MQ]$Ta(OAr)_3(PMe_3)$ (**8**)

Crystals of $[\eta^2(N,C)$-6MQ]$Ta(OAr)_3(PMe_3)$ (**8**) marginally suitable for an X-ray structural determination were obtained with great difficulty from toluene/heptane solution at −35°C. Figure 2 presents the molecular structure of **8** and Tables 2 and 3 present selected crystal and structural data. Although the difficulty in obtaining high quality crystals of **8** and the solvent disorder problems prevented our obtaining very precise structural data, several general features of the $\eta^2(N,C)$ bond mode can be established in this compound. The location of the methyl group in the 6-methylquinoline ligand unambiguously confirms its $\eta^2(N,C)$, rather than $\eta^2(C,C)$, bonding mode. Considering the $\eta^2(N,C)$ ligand as occupying a single coordination site, the complex is seen to adopt an approximate square pyramidal geometry with the $\eta^2(N,C)$ ligand π bonded in the axial site. Two disordered, partially occupied heptane molecules included in the crystal limited the precision of the structure, therefore caution must be exercised in interpreting and drawing conclusions from any data. However, the $\eta^2(N,C)$ bonding mode does appear to interrupt the aromaticity of the heterocyclic ring as C(11)–C(12) = 1.30 (1)Å, while the C—C bonds in the aryloxide phenyl groups (which constitute a good measure of aromaticity) average 1.38 (2)Å. The Ta—C(10) = 2.208 (9) Å, Ta—N = 1.961 (7) Å, and C(10)—N = 1.44 (1) Å bond distances imply the Ta^V "metallaaziridine" formulation described

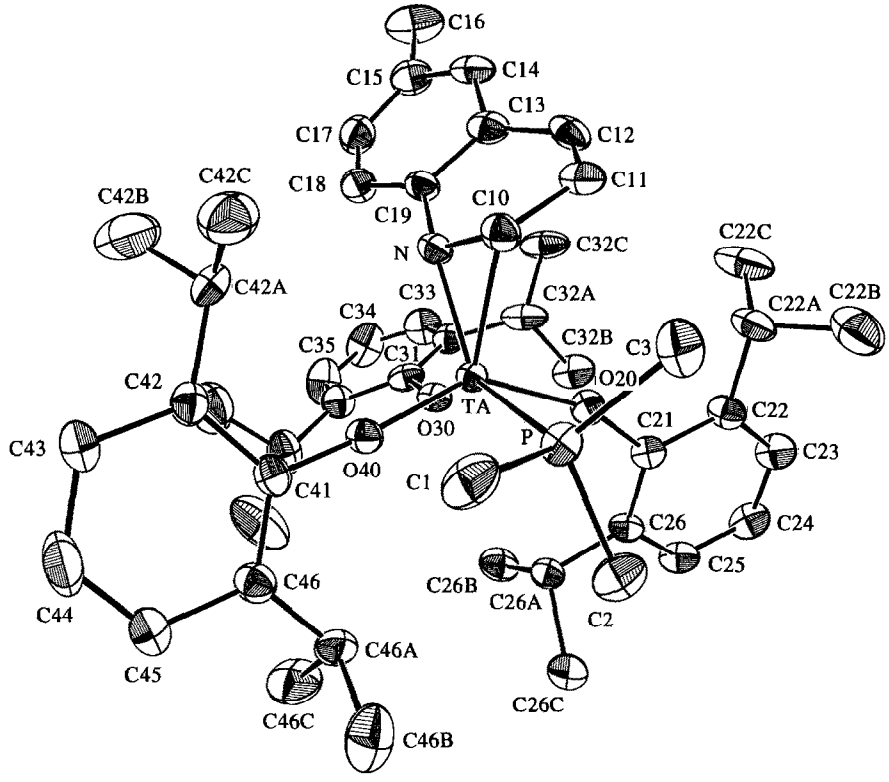


Fig. 2. Molecular structure of $[\eta^2(N,C)$-6MQ]Ta$(OAr)_3(PMe_3)$ (**8**) (Ar = 2,6-diisopropylphenyl) with atoms shown as 20% thermal ellipsoids.

previously.[46] Heterocycle distortions are also evident since N is below and C(10) above the best 6-methylquinoline ligand plane. The angle between the best 6MQ plane and the N—C(10)—Ta plane is 131.1 (4)° [compared to 117.6 (5)° in the pyridine complex $[\eta^2(N,C)$-2,4,6-NC_5H_2-*t*-Bu_3]Ta$(OAr)_2$ Cl],[33b] suggesting an orientation of the Ta$(OAr)_3$ (PMe_3) moiety which is not interacting with the remainder of the heterocyclic π system. Consistent with this suggestion are the Ta···C(11) and Ta···C(19) distances, both of which are 3.22 (1) Å. The best canonical structure for this complex is therefore the one presented in Scheme 2.

Structural study of $[\eta^2$(N,C)-6MQ]Ta$(OAr)_2$Cl (OEt_2) (**9**)

Although a *great deal* of effort was expended in attempts to grow crystals of $[\eta^2(N,C)$-6MQ]Ta$(OAr)_2$Cl(OEt_2) (**9**) suitable for an X-ray structure, a sample acceptable for diffraction studies was obtained only by a happenstance crystallization directly from the Et_2O (NaHg reduction) reaction solution at −35°C. The molecular structure of $[\eta^2(N,C)$-6MQ]Ta$(OAr)_2$Cl(OEt_2) is presented in Fig. 3, and Tables 2 and 4 summarize crystal and structural data. Again, the $\eta^2(N,C)$ bonding mode of the 6-methylquinoline ligand is unambiguously determined through the location of the methyl substituent on the ring. Unlike **8** described above, $[\eta^2(N,C)$-6MQ]Ta$(OAr)_2$Cl (OEt_2) (**9**) is best described as an overall trigonal bipyramidal structure with the $\eta^2(N,C)$ ligand occupying an axial position *trans* to the coordinated ether molecule [N,C—Ta—O(43) = 170.4 (2)°]. Because the crystal was weakly diffracting and since the ether molecule was disordered, bond distances and angles have high uncertainties, again requiring caution in the interpretation of these values. However, in this structure, interruption of aromaticity in the heterocyclic ring is also apparent. The C(3)—C(4) bond distance of 1.31 (2) Å can be compared to the aromatic C—C bonds in the aryloxide ligands, which average 1.38 (2) Å. Bond distances of Ta—N(1) = 1.95 (1) Å, Ta—C(2) = 2.13 (2) Å, and the N(1)—C(2) distance of 1.41 (2) Å are consistent with tantalum attaining its highest oxidation state and a metallaaziridine structure. The angle between the best 6-methylquinoline ligand plane and the N—C(2)—Ta plane is 129.3 (4)°, intimating a Ta$(OAr)_2Cl(OEt_2)$ fragment which is not interacting with the rest of the heterocyclic π system. The Ta···C(3) distance of 3.22 (1) Å and Ta···C(10) distance of 3.18 (1) Å are

Table 2. Details of the X-ray diffraction studies for $[\eta^2(N,C)$-6MQ]$Ta(OAr)_3(PMe_3)$ (**8**) and $[\eta^2(N,C)$-6MQ]$Ta(OAr)_2Cl(OEt_2)$ (**9**)

Parameter	Compound **8**	Compound **9**
Crystal parameters		
Molecular formula	$TaPO_3NC_{49}H_{69}$	$TaClO_3NC_{38}H_{53}$
Molecular weight	932.02	788.25
$F(000)$	3856	1608
Crystal colour	yellow	red
Space group	monoclinic $C2_1/c$ (No. 15)	monoclinic $P2_1/n$ (No. 14)
Unit cell volume (Å^3)	10702 (2)	3828 (9)
a (Å)	32.849 (3)	12.059 (9)
b (Å)	19.579 (2)	17.975 (14)
c (Å)	23.822 (2)	17.949 (13)
β (°)	135.69 (49)	100.29 (3)
Z	8	4
D (calc) (g cm^{-3})	1.16	1.37
Crystal dimensions (mm)	$0.35 \times 0.17 \times 0.17$	$0.12 \times 0.15 \times 0.45$
ω width (°)	0.25	0.30
Absorption coefficient (cm^{-1})	20.9	29.4
Data collection temp (°C)	20 ± 1	22 ± 1
Data collection and reduction		
Diffractometer	Enraf–Nonius CAD4	Syntex $P2_1$, Crystal Logics
Monochromator	graphite crystal, incident beam	graphite crystal, incident beam
Mo K_α radiation, λ (Å)	0.70930	0.71073
2θ range (°)	2–50	2–50
Octants collected	$+h, +k, \pm l$	$+h, +k, \pm l$
Scan type	ω–2θ	ω–2θ
Scan speed (° min^{-1})	1–7	3.0
Scan width (°)	θ scan width $= 0.6 + 0.140 \tan\theta$	from $(2\theta K\alpha_1 - 1.3)$ to $(2\theta K\alpha_2 + 1.6)$
Total no. of reflns measd	10,919 (9393 unique)	7471 (6754 unique)
Corrections	Lorentz-polarization Linear decay (from 0.995 to 1.437 on I) Reflection averaging (agreement on $I = 1.7\%$) Ψ-scan absorption (from 0.92 to 1.00 on I)	Lorentz-polarization Anisotropic decay (from 0.986 to 1.238 on I) Reflection averaging (agreement on $I = 2.2\%$) Ψ-scan absorption
Solution and refinement		
Solution	Patterson method	Patterson method
Refinement	Full-matrix least-squares	Full-matrix least-squares
Reflns used in refinement; $I > 3\sigma(I)$	5289	2741
Parameters refined	496	271
R	0.054	0.044
R_w	0.087	0.051
E.s.d. of obs. of unit weight	2.88	1.26
Convergence, largest shift	0.45σ	0.31σ
Δ/σ (max) (e^{-1} Å^{-3})	1.57 (17)	0.74 (10)
Δ/σ (min) (e^{-1} Å^{-3})	−0.81 (17)	−0.19 (10)
Computer hardware	VAX	VAX
Computer software	SDP/VAX (Enraf–Nonius)	MolEN (Enraf–Nonius)

Table 3. Selected bond distances (Å) and bond angles (°) in $[\eta^2(N,C)\text{-6MQ}]Ta(OAr)_3(PMe_3)$ (**8**)[a,b]

Bond distances			
Ta—N	1.961(7)	C(13)—C(14)	1.49(2)
Ta—C(10)	2.208(9)	C(13)—C(19)	1.40(1)
Ta—P	2.685(2)	C(14)—C(15)	1.30(2)
Ta—O(20)	1.904(6)	C(15)—C(16)	1.51(1)
Ta—O(30)	1.943(6)	C(15)—C(17)	1.39(2)
Ta—O(40)	1.894(5)	C(17)—C(18)	1.35(1)
N—C(10)	1.44(1)	C(18)—C(19)	1.30(1)
N—C(19)	1.41(1)	O(20)—C(21)	1.42(1)
C(10)—C(11)	1.42(1)	O(30)—C(31)	1.41(1)
C(11)—C(12)	1.30(1)	O(40)—C(41)	1.387(9)
C(12)—C(13)	1.48(2)		

Bond angles[b]			
N,C—Ta—P	96.93(9)	C(10)—Ta—O(30)	128.2(3)
N,C—Ta—O(20)	109.5(3)	C(10)—Ta—O(40)	109.3(3)
N,C—Ta—O(30)	111.0(2)	N—Ta—C(10)	39.7(3)
N,C—Ta—O(40)	106.9(2)	Ta—C(10)—N	60.8(4)
P—Ta—O(20)	77.3(2)	Ta—N—C(10)	79.4(5)
P—Ta—O(30)	151.9(2)	Ta—N—C(19)	145.0(6)
P—Ta—O(40)	80.1(2)	Ta—C(10)—C(11)	123.4(6)
O(20)—Ta—O(30)	90.5(2)	N—C(10)—C(11)	115.4(8)
O(20)—Ta—O(40)	139.0(3)	C(10)—C(11)—C(12)	117.(1)
O(30)—Ta—O(40)	93.7(2)	C(11)—C(12)—C(13)	126.(1)
N—Ta—P	116.8(2)	C(12)—C(13)—C (19)	117.(1)
N—Ta—O(20)	118.7(3)	C(13)—C(19)—N	115(1)
N—Ta—O(30)	91.3(3)	C(19)—N—C(10)	122.3(7)
N—Ta—O(40)	102.0(3)	Ta—O(20)—C(21)	158.3(5)
C(10)—Ta—P	79.3(3)	Ta—O(30)—C(31)	156.2(5)
C(10)—Ta—O(20)	99.6(3)	Ta—O(40)—C(41)	174.5(6)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.
[b] The abbreviation N,C represents the midpoint of the N—C(10) bond.

supportive of this argument. The aryloxide ligands display rather different Ta—O—C_{ipso} bond angles of 152.8 (8) and 175.3 (9) Å, although both ligands occupy equatorial sites of the trigonal bipyramid. In general, the heterocyclic rings of **8** and **9** compare fairly well in their similar degree of π localization as predicted from their canonical structures, although the benzannulated rings cannot be correlated due to the imprecision of the structures.

Preparation and properties of d^1, η^1(N) *heterocyclic adducts*

As described above, the isolation of the bis (aryloxide) species $[\eta^2(N,C)\text{-6MQ}]Ta(OAr)_2Cl(OEt_2)$ (**9**) must be accomplished by the *rapid, two-electron* reduction of the d^0 starting complex. If the *second* electron transfer in this two-electron reduction is not carried out rapidly enough, the intermediate d^1 complex acts as an effective scavenger of 6MQ from solution and the stable, six-coordinate Ta^{IV} complex $[\eta^1(N)\text{-6MQ}]_2Ta(OAr)_2Cl_2$ is isolated. Thus, the series of d^1 compounds $[\eta^1(N)\text{-QUIN}]_2Ta(OAr)_2Cl_2$ (**10**), $[\eta^1(N)\text{-6MQ}]_2Ta(OAr)_2Cl_2$ (**11**), and the pyridine adduct $[\eta^1(N)\text{-py}]_2Ta(OAr)_2Cl_2$ (**12**) are all available from the one-electron reduction of $Ta(OAr)_2Cl_3(OEt_2)$ in the presence of 2 equiv. of the corresponding heterocycle (Scheme 4). A preliminary structural study of $[\eta^1(N)\text{-py}]_2Ta(OAr)_2Cl_2$ has revealed it to exist as the "all-*trans*" isomer; we assume compounds **10** and **11** are analogous. Based upon these observations, the sequence of reactions leading to d^0, d^1 and d^2 heterocyclic adducts is proposed in equations (1)–(5), where the 6MQ complexes specifically have been isolated in each oxidation state. These observations are consistent with the formation of an intermediate d^1 complex $[\eta^1(N)\text{-6MQ}]Ta(OAr)_2Cl_2(OEt_2)_n$, where $n = 0$ or 1, which partitions between two

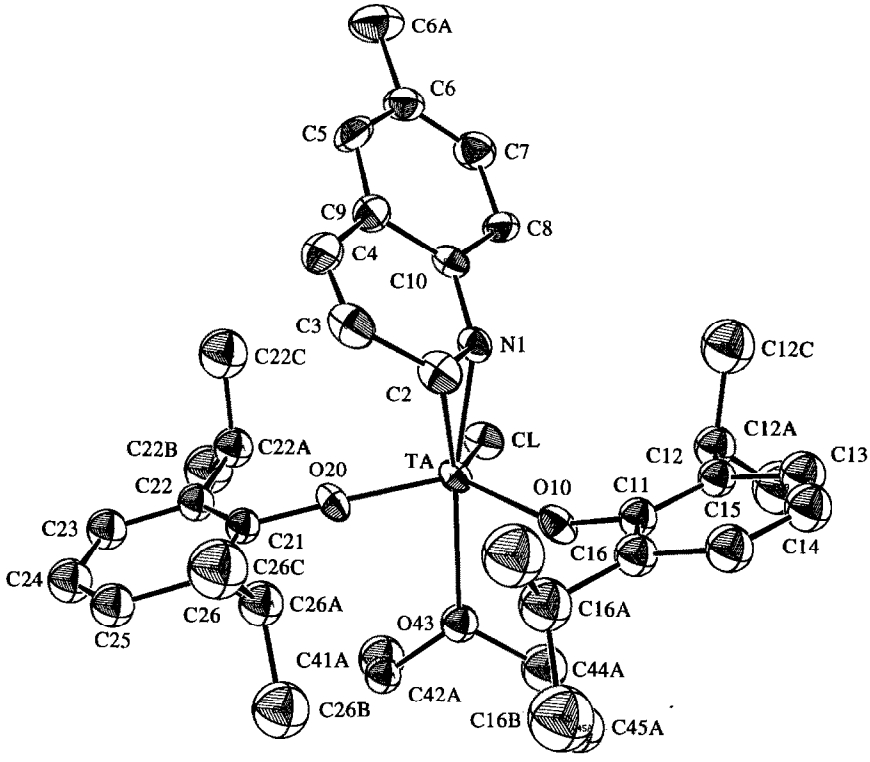


Fig. 3. Molecular structure of $[\eta^2(N,C)\text{-6MQ}]Ta(OAr)_2Cl(OEt_2)$ (**9**) (Ar = 2,6-diisopropylphenyl) with atoms shown as 20% probability ellipsoids.

further reactions—either another one-electron reduction, equation (4), or coordination of another 6MQ ligand, equation (5):

$$Ta(OAr)_2Cl_3(OEt_2) + 6MQ \rightleftharpoons [\eta^1(N)\text{-6MQ}]Ta(OAr)_2Cl_3 + Et_2O \quad (1)$$

$$[\eta^1(N)\text{-6MQ}]Ta(OAr)_2Cl_3 + e^- \longrightarrow [\eta^1(N)\text{-6MQ}]Ta(OAr)_2Cl_2 \quad (2)$$

$$[\eta^1(N)\text{-6MQ}]Ta(OAr)_2Cl_2 + Et_2O \rightleftharpoons [\eta^1(N)\text{-6MQ}]Ta(OAr)_2Cl_2(OEt_2) \quad (3)$$

$$[\eta^1(N)\text{-6MQ}]Ta(OAr)_2Cl_2(OEt_2)_n + e^- \longrightarrow [\eta^2(N,C)\text{-6MQ}]Ta(OAr)_2Cl(OEt_2) \quad (4)$$

$$[\eta^1(N)\text{-6MQ}]Ta(OAr)_2Cl_2(OEt_2)_n + 6MQ \longrightarrow [\eta^1(N)\text{-6MQ}]_2Ta(OAr)_2Cl_2 \quad (5)$$

The displacement of a chloride ligand by a 6MQ ligand in $[\eta^1(N)\text{-6MQ}]Ta(OAr)_2Cl_3$ to form an intermediate of the type $\{[\eta^1(N)\text{-6MQ}]_2Ta(OAr)_2Cl_2\}^+$ is not likely based upon the observed ligand exchange reactions described above.

These paramagnetic d^1 compounds are characterized by eight line ESR spectra in solution with $g_{avg} = 1.82$ and $A(^{181}Ta) \approx 225$ G, diagnostic for hyperfine coupling with ^{181}Ta ($I = 7/2$). Cyclic voltammetry measurements of these species (0.1 M *n*-Bu_4NPF_6 in THF) revealed that they all exhibit an irreversible, one-electron oxidation process near 0.4 V vs Ag/AgCl, although the ill-defined electrochemical processes following this oxidation suggest the resulting cation is unstable under these conditions. In addition, the pyridine adduct displayed an irreversible reduction at $E_{pc} = -1.25$ V vs Ag/AgCl under these same conditions. Finally, we should note that attempts to reduce $[\eta^1(N)\text{-6MQ}]_2Ta(OAr)_2Cl_2$ by one electron afforded only small amounts of the corresponding d^2 complex $[\eta^2(N,C)\text{-6MQ}]Ta(OAr)_2Cl(OEt_2)$ (**9**), while attempts to reduce the quinoline and pyridine d^1 species yielded only intractable oils.

Hydrogenation studies of $[\eta^2(N,C)\text{-QUIN}]Ta(OAr)_3$

The structural data in complexes **8** and **9** suggest the aromaticity of the nitrogen heterocycle is diminished by bonding $\eta^2(N,C)$ to the metal centre; therefore we selected one of the η^2 compounds to examine under hydrogenation conditions. Since the instability of **5** towards free quinoline precluded *catalytic* hydrogenation studies, and since the PMe_3 adducts **7** and **8** showed much lower reactivity than their base-free counterparts, we examined the hydrogenation reactivity of $[\eta^2(N,C)\text{-QUIN}]Ta$

Table 4. Selected bond distances (Å) and bond angles (°) in $[\eta^2(N,C)\text{-6MQ}]Ta(OAr)_2Cl(OEt_2)$ (**9**)[a,b]

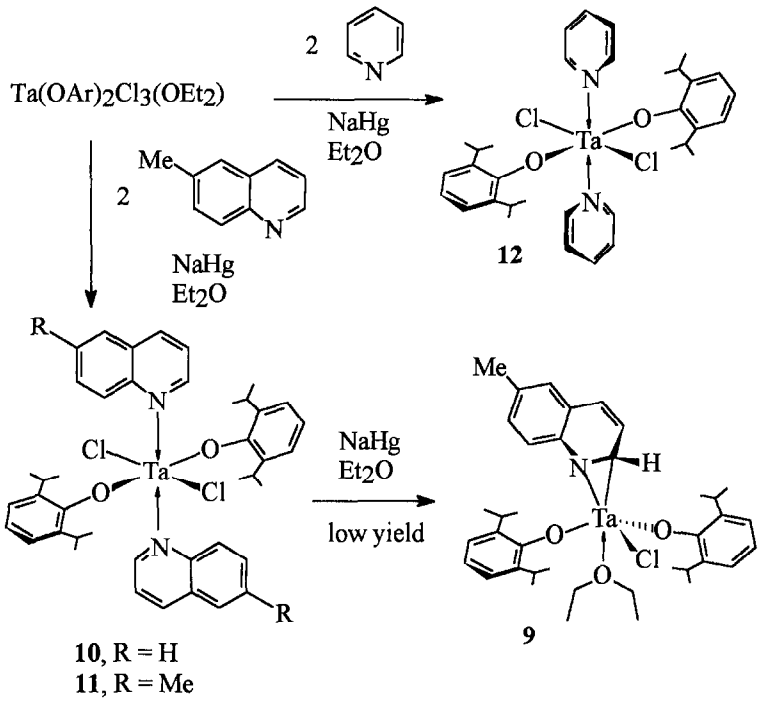
Bond distances			
Ta—N(1)	1.95(1)	C(9)—C(10)	1.44(2)
Ta—C(2)	2.13(2)	C(9)—C(5)	1.41(2)
Ta—Cl	2.372(3)	C(5)—C(6)	1.35(2)
Ta—O(10)	1.870(9)	C(6)—C(6A)	1.49(2)
Ta—O(20)	1.869(8)	C(6)—C(7)	1.35(2)
Ta—O(43)	2.346(9)	C(7)—C(8)	1.40(2)
N(1)—C(2)	1.41(2)	C(8)—C(10)	1.40(2)
N(1)—C(10)	1.41(2)	O(10)—C(11)	1.38(1)
C(2)—C(3)	1.47(2)	O(20)—C(21)	1.39(1)
C(3)—C(4)	1.31(2)	O(43)—C(42A)	1.50(3)
C(4)—C(9)	1.43(2)	O(43)—C(44A)	1.55(4)
Bond angles[b]			
N,C—Ta—Cl	104.42(8)	C(2)—Ta—O(43)	152.6(5)
N,C—Ta—O(10)	94.6(2)	N(1)—Ta—C(2)	40.1(5)
N,C—Ta—O(20)	100.9(2)	Ta—C(2)—N(1)	63.3(8)
N,C—Ta—O(43)	170.4(2)	Ta—N(1)—C(2)	76.6(9)
Cl—Ta—O(10)	112.3(3)	Ta—N(1)—C(10)	141.7(9)
Cl—Ta—O(20)	105.1(3)	Ta—C(2)—C(3)	127.(1)
Cl—Ta—O(43)	84.1(3)	N(1)—C(2)—C(3)	116.(1)
O(10)—Ta—O(20)	134.2(4)	C(2)—C(3)—C(4)	120.(2)
O(10)—Ta—O(43)	77.8(4)	C(3)—C(4)—C(9)	125.(2)
O(20)—Ta—O(43)	80.8(3)	C(4)—C(9)—C(10)	115.(2)
N(1)—Ta—Cl	83.8(3)	C(9)—C(10)—N(1)	120.(1)
N(1)—Ta—O(10)	99.6(4)	C(10)—N(1)—C(2)	121.(1)
N(1)—Ta—O(20)	110.1(4)	Ta—O(10)—C(11)	152.8(8)
N(1)—Ta—O(43)	165.5(4)	Ta—O(20)—C(21)	175.3(9)
C(2)—Ta—Cl	123.3(5)	Ta—O(43)—C(42A)	126.(1)
C(2)—Ta—O(10)	89.5(5)	Ta—O(43)—C(44A)	123.(2)
C(2)—Ta—O(20)	91.5(5)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.
[b] The abbreviation N,C represents the midpoint of the N(1)—C(2) bond.

$(OAr)_3$ (**5**) in the absence of excess quinoline. Extremely mild hydrogenation conditions were employed (room temperature, Et_2O solution, 125 psi H_2, 24 h), after which the solution was quenched with H_2O and the organic products were extracted and examined by GC-MS. We also subjected solutions of free QUIN and $[\eta^1(N)\text{-QUIN}]Ta(OAr)_3Cl_2$ (**1**) to identical hydrogenation and work-up conditions. While the reactions of free QUIN or **1** with hydrogen show *no reduction* of quinoline occurred under these conditions (only quinoline and HOAr were observed upon work-up), $[\eta^2(N,C)\text{-QUIN}]Ta(OAr)_3$ (**5**) reacts with hydrogen to afford 1,2,3,4-tetrahydroquinoline (THQ) as the principal hydrogenation product; *no* decahydroquinoline was observed as a result of hydrogenation of the benzene ring. Semiquantitative GC-MS data (see Experimental) reveal that the conversion of the $\eta^2(N,C)$-QUIN ligand in **5** to THQ is roughly 45% after 24 h under these exceptionally mild conditions. The other detectable products from the hydrogenation are unreacted QUIN (formed upon quenching unreacted **5**) and a minor amount of 2,2′-biquinoline (up to 5%), which most likely stems from the thermal decomposition of **5** over time (*vide supra*).[45]

DISCUSSION

Hydrogen consumption represents a *major* cost of hydrotreating and HDN is a principal H_2 consumer, since achieving nitrogen removal typically requires complete hydrogenation of all the aromatic rings of the molecule. A process which could effect HDN selectively, i.e. without complete hydrogenation of the substrate, is highly desirable. In addition, this lack of selectivity is manifested in the hydrogenation of aromatic compounds which are *not* heterocyclic in nature, further lowering the quality (octane) of the final product. Finally,



Scheme 4.

although HDN is carried out simultaneously with other hydrotreating reactions (e.g. hydrodesulphurization (HDS) and hydrodeoxygenation (HDO)), hydrotreating parameters are usually *optimized* for only one of these processes, most often HDS.[1-3] Thus, catalysts and conditions which are optimum for removing sulphur are usually not optimum for HDN, so nitrogen removal is not an efficient process as it is currently practised.

The present model system displays reactions which address these current limitations in HDN catalysis. By the *selective* binding of d^2 $Ta(OAr)_nCl_{3-n}$ moieties to the heterocycles in the $\eta^2(N,C)$ mode, the aromaticity of the heterocyclic ring *alone* is disrupted, a feature which allows it to undergo hydrogenation selectively. The structures we have characterized are similar to Wolczanski's $[\eta^2(N,C)\text{-}NC_5H_5]Ta(silox)_3$[32] complex (silox = OSi-*t*-Bu_3), which is also bonded through the pyridine nitrogen and an α-carbon, but distinctively different from Taube's $\eta^2(C,C)$ bonded pyridine complexes such as $[(\eta^2(C,C)\text{-lutidene})Os(NH_3)_5]^{2+}$.[34] Although Wolczanski has described an η^2 benzene complex of $Ta(silox)_3$, we have observed these d^2 tantalum aryloxide species to bind nitrogen heterocycles $\eta^2(N,C)$ only, never $\eta^2(C,C)$ as in Taube's compounds. Therefore, this system displays a highly desirable property one would impart to the industrially employed catalysts: selectivity for inducing reactivity at the heterocyclic ring only.

The structures of $[\eta^2(N,C)\text{-6MQ}]Ta(OAr)_3(PMe_3)$ (**8**) and $[\eta^2(N,C)\text{-6MQ}]Ta(OAr)_2Cl(OEt_2)$ are clearly indicative of the Ta^V "metallaaziridine" description of bonding,[46] rather than a simple $Ta^{III}-\pi$ complex formulation. These structures therefore suggest that a metal–ligand π interaction ($d\pi \Rightarrow p\pi^*$) is preferred over the rather inefficient δ backbonding ($d\delta \Rightarrow$ arene δ^* {arene π^* LUMO}) to allow the metal to attain its highest oxidation state. This conclusion was also obtained in Wolczanski's theoretical study of related $[\eta^2(N,C)\text{-}NC_5H_5]Ta(OH)_3$.[32a] The η^2 coordination and the misshapen pyridine ligand indicate an obvious disruption of aromaticity and therefore must extract a high energetic price,[47] but it apparently can be afforded from the gains made in π backbonding.

CONCLUSIONS

Despite its singular importance in producing high quality, low-cost fuels and feedstocks, HDN catalysis is significantly less well-studied than HDS. The development of our model system using tantalum aryloxide complexes has been directed towards gaining a more fundamental understanding of HDN reactions and allows us to draw the following conclusions.

(i) Using aryloxide-supported tantalum complexes, we have demonstrated the $\eta^2(N,C)$ coordination mode of relevant HDN substrates such as quinolines and have substantiated the correlation between oxidation state and preferred bonding mode as follows: d^0 $[\eta^1(N)]$, d^1 $[\eta^1(N)]$ and d^2 $[\eta^2(N,C)]$.

(ii) We have established an $\eta^1(N) \rightarrow \eta^2(N,C)$ bonding mode conversion in aryloxide-supported quinoline complexes upon the metal's reduction from the d^0 to the d^2 oxidation state. While an intermediate d^1 $[\eta^1(N)]$ compound may be further reduced to its d^2 $[\eta^2(N,C)]$ analogue, if another heterocycle substrate coordinates *prior to* the second electron transfer, this reduction is exceedingly inefficient.

(iii) Structural studies have demonstrated the disruption of aromaticity of the heterocyclic ring in the d^2 $[\eta^2(N,C)]$ compounds. Because the $\eta^2(C,C)$ coordination mode has not been observed in this system, the d^2 $Ta(OAr)_nCl_{3-n}$ moieties are capable of *selectively* interfering with the aromaticity of the heterocyclic ring in polyaromatic substrates.

(iv) Under extremely mild hydrogenation conditions, only the d^2 $[\eta^2(N,C)]$ quinoline compounds are readily hydrogenated; neither the d^0 $[\eta^1(N)]$, the d^1 $[\eta^1(N)]$, nor uncoordinated quinolines are hydrogenated under these conditions. Furthermore, the hydrogenation of the $\eta^2(N,C)$ compounds is selective for the heterocyclic ring as only 1,2,3,4-tetrahydroquinoline is observed with no decahydroquinoline formed.

(v) When this study is considered alongside our discovery[42] of the facile, regioselective C—N bond scission of an $\eta^2(N,C)$ pyridine complex (namely $[\eta^2(N,C)$-2,4,6-NC_5H_2-*t*-$Bu_3]Ta(OAr)_2Cl$), these compounds may be considered as highly relevant models for fundamental HDN reactions and substrate–catalyst interactions.

EXPERIMENTAL

General details

All experiments were performed under a nitrogen atmosphere either by standard Schlenk techniques[48] or in a Vacuum Atmospheres HE-493 drybox at room temperature (unless otherwise indicated). Solvents were distilled under N_2 from an appropriate drying agent[49] and were transferred to the drybox without exposure to air. The "cold" solvents used to wash isolated solid products were typically cooled to *ca* −30°C before use. NMR solvents were passed down a short (5–6 cm) column of activated alumina prior to use. In all preparations, Ar = 2,6-diisopropylphenyl(2,6-C_6H_3-*i*-Pr_2), QUIN = quinoline (NC_9H_7) and 6MQ = 6-methylquinoline ($NC_{10}H_9$).

Physical measurements

^1H (250 MHz) and ^{13}C (62.9 MHz) NMR spectra were recorded at probe temperature (unless otherwise specified) on a Bruker WM-250 or Bruker AM-250 spectrometer in C_6D_6 or toluene-d_8 solvent. Chemical shifts are referenced to protio impurities (δ 7.15, C_6D_6; 2.09, toluene-d_8) or solvent ^{13}C resonances (δ 128.0, C_6D_6; 20.4, toluene-d_8) and are reported downfield of Me_4Si. Carbon assignments were assisted by APT or gated $^{13}C\{^1H\}$ decoupled spectra. ESR spectra were recorded on a Bruker ESP 300E spectrometer at room temperature in toluene or benzene solution. Infrared spectra were recorded in Et_2O solution between 4000 and 400 cm^{-1} using a Nicolet 510P FTIR spectrometer and were not assigned, but recorded as fingerprint spectra. Cyclic voltammetry experiments were performed in a nitrogen filled drybox using a Cypress Systems CSY-1 voltammograph and were recorded on a Hewlett Packard recorder. Measurements were taken at a Pt-disk electrode in THF solutions containing 0.1 M *n*-Bu_4NPF_6 as supporting electrolyte. Voltammograms were recorded at room temperature at a scan rate of 100 mV s^{-1} and E_p values are referenced to Ag/AgCl and are uncorrected for junction potentials. Electron ionization mass spectra (70 eV) were recorded to $m/z = 999$ on a Hewlett Packard 5890 gas chromatograph, 5970 mass selective detector and RTE-6/VM data system. For the hydrogenation studies, the sample was introduced into the mass spectrometer by a Hewlett Packard model 5890 gas chromatograph equipped with an HP-5 column. GC-MS response factors for quinoline and 1,2,3,4-tetrahydroquinoline were determined relative to tetradecane internal standard and employed to approximately quantify these compounds after hydrolysis of the $[\eta^2(N,C)$-QUIN] $Ta(OAr)_3$ hydrogenation reaction. Coefficients for the extraction of quinoline and 1,2,3,4-tetrahydroquinoline under the work-up conditions were also determined with this method and were factored into the final product analysis. Microanalytical samples were handled under nitrogen and were combusted with WO_3 (Desert Analytics, Tucson, Arizona).

Starting materials

$Ta(OAr)_3Cl_2(OEt_2)$,[50] $Ta(OAr)_2Cl_3(OEt_2)$[41b] and $(\eta^6$-$C_6Me_6)Ta(OAr)_2Cl$[51] were prepared by the literature procedures. Trimethylphosphine was prepared and purified by the literature procedure,[52] with the modification of using MeMgI rather than

MeMgBr in the preparation. Quinoline (Fisher) was distilled from CaH_2 prior to use. 6-Methylquinoline (Aldrich) and pyridine (Mallinckrodt) were both distilled prior to use and pyridine was stored over 4 Å molecular sieves.

Preparations

$[\eta^1(N)$-QUIN]$Ta(OAr)_3Cl_2$ (**1**). Neat quinoline (0.70 cm^3, 5.9 mmol) was added to a rapidly stirred solution of $Ta(OAr)_3Cl_2(OEt_2)$ (5.00 g, 5.82 mmol) in *ca* 40 cm^3 of pentane. The pale yellow solution slowly became cloudy as a yellow precipitate formed. After 1 h the resulting yellow solid was filtered off, washed with cold pentane (*ca* 40 cm^3), and dried *in vacuo* to provide 4.83 g (5.29 mmol, 91%) of $[\eta^1(N)$-QUIN]$Ta(OAr)_3Cl_2$ (**1**). Samples of $[\eta^1(N)$-QUIN]$Ta(OAr)_3Cl_2$ (**1**) obtained in this fashion were found to be analytically pure. ^1H NMR (toluene-d_8, 373 K): δ 9.50 (d, $J = 5.1$ Hz, 1 H, H(2), QUIN), 9.09 (d, $J = 8.9$ Hz, 1 H, H(8), QUIN), 7.64 (d, $J = 8.1$ Hz, 1 H, H(4), QUIN), 7.30 (d, $J = 8.0$ Hz, 1 H, H(5), QUIN), 7.05 and 6.86 (pseudo d and t, respectively (A_2B mult), 9 H total, H_{aryl}, OAr), 7.11–6.96 (overlapping m, 2 H total, H(6) and H(7), QUIN), 6.69 (dd, 1 H, H(3), QUIN), 3.93 (spt, 6 H, C*H*Me_2), 1.03 (d, 36 H, CH*Me*$_2$). Partial ^1H NMR (C_6D_6, ambient probe temp): δ 9.63 (d, $J = 5.2$ Hz, 1 H, H(2), QUIN), 9.32 (d, $J = 8.5$ Hz, 1 H, H(8), QUIN), 7.35 (d, $J = 8.1$ Hz, 1 H, H(4), QUIN), 6.82 (partially obscured t, $J \approx 8$ Hz, 1 H, H(6), QUIN), 6.31 (dd, $J = 5.2$ and 8.2 Hz, 1 H, H(3), QUIN). At ambient temperature, all of the OAr resonances appear as broad envelopes of signals; however, the QUIN resonances listed are diagnostic for this compound. Note that H(5) and H(7) QUIN resonances are obscured [and H(6) *partially* hidden] by the broad OAr aryl signals. ^{13}C NMR (toluene-d_8, 373 K): δ 156.9 (C_{ipso}, OAr), 155.4 (C(2), QUIN), 146.7 (C(9), QUIN), 141.0 (C_o, OAr), 131.2, 130.0, and 129.8 (C(5), C(8), and C(10), QUIN), 128.4 and 127.6 (C(6) and C(7), QUIN), 124.4 (sh, C_p, OAr), 124.3 (C_m, OAr), 120.7 (C(3), QUIN), 26.7 (*C*HMe_2), 24.8 (CH*Me*$_2$). One QUIN carbon is not observed; we believe C(4) is coincident with the C_o (OAr) resonance at δ 141.0 or the solvent resonance at δ 137.5. Calc. for $C_{45}H_{58}Cl_2NO_3Ta$: C, 59.21; H, 6.40, N, 1.53. Found: C, 59.33; H, 6.64; N, 1.46.

$[\eta^1(N)$-6MQ]$Ta(OAr)_3Cl_2$ (**2**). Slightly over 1 equiv. of 6-methylquinoline (0.84 cm^3, 6.24 mmol) was added neat to a rapidly stirred solution of $Ta(OAr)_3Cl_2(OEt_2)$ (5.11 g, 5.96 mmol) in *ca* 40 cm^3 of pentane. The pale yellow solution gradually became cloudy as a yellow precipitate formed and after 1 h the resulting yellow solid was filtered off, washed with cold pentane (*ca* 40 cm^3), and dried *in vacuo* to afford 5.02 g (5.42 mmol, 91%) of $[\eta^1(N)$-6MQ]$Ta(OAr)_3Cl_2$ (**2**) as an analytically pure, pale yellow solid. ^1H NMR (toluene-d_8, 373 K): δ 9.24 (br, 1 H, H(2), 6MQ), 8.83 (br d, $J = 9.0$ Hz, 1 H, H(8), 6MQ), 7.64 (d, $J = 8.0$ Hz, 1 H, H(4), 6MQ), 7.05 and 6.85 (pseudo d and t, respectively (A_2B mult), 9 H total, H_{aryl}, OAr), 7.11 and 6.96 (br, 1 H each, H(5) and H(7), 6MQ, partially obscured by OAr H_{aryl} signal), 6.74 (dd, $J = 5.4$ and 8.2 Hz, 1 H, H(3), 6MQ), 3.96 (br, 6 H, C*H*Me_2), 2.03 (s, 3 H, CH_3, 6MQ), 1.06 (br, 36 H, CH*Me*$_2$). ^1H NMR (C_6D_6, 333 K): δ 9.62 (br, 1 H, H(2), 6MQ), 9.18 (br, 1 H, H(8), 6MQ), 7.59 (d, $J = 8.0$ Hz, 1 H, H(4), 6MQ), 7.20–6.94 (overlapping A_2B mult and broad signals, 11 H total, H_{aryl} (OAr) and H(5)/H(7), 6MQ), 6.62 (br m, 1 H, H(3), 6MQ), 4.13 (br, 6 H, C*H*Me_2), 1.97 (s, 3 H, CH_3, 6MQ), 1.19 (br, 36 H, CH*Me*$_2$). At ambient temperature, all of the OAr resonances appear as broad envelopes of signals and H(5) and H(7) 6MQ resonances are obscured by the broad OAr H_{aryl} signals. ^{13}C NMR (toluene-d_8, 373 K): δ 156.8 (C_{ipso}, OAr), 152.6 (C(2), 6MQ), 144.1 (C(9), 6MQ), 141.1 and 140.7 (C(4), 6MQ and C_o, OAr), 139.2 (C(6), 6MQ), 138.3, 133.9, 130.1, and 127.2 (C(5), C(7), C(8), and C(10), 6MQ), 124.2 (coincident C_m and C_p, OAr), 120.8 (C(3), 6MQ), 26.6 (*C*HMe_2), 24.9 (CH*Me*$_2$), 24.6 (CH_3, 6MQ) Calc. for $C_{46}H_{60}Cl_2NO_3Ta$: C, 59.61; H, 6.52; N, 1.51. Found: C, 60.37; H, 6.70; N, 1.27.

$[\eta^1(N)$-6MQ]$Ta(OAr)_2Cl_3$ (**4**). A slight excess of 6-methylquinoline (0.408 cm^3, 3.03 mmol) was added neat to a rapidly stirred slurry of $Ta(OAr)_2Cl_3(OEt_2)$ (2.00 g, 2.79 mmol) in *ca* 30 cm^3 of pentane. The reaction developed into a thick slurry over 15–20 min as a bright yellow precipitate formed. After 24 h the bright yellow solid was collected by filtration, washed with cold pentane, and dried *in vacuo* to provide 1.94 g (2.47 mmol, 89%) of $[\eta^1(N)$-6MQ]$Ta(OAr)_2Cl_3$ (**4**). Samples of $[\eta^1(N)$-6MQ]$Ta(OAr)_2Cl_3$ (**4**) obtained in this fashion were found to be analytically pure. ^1H NMR (C_6D_6): δ 9.78 (d, $J = 5.2$ Hz, 1 H, H(2), 6MQ), 9.08 (d, 1 H, H(8), 6MQ), 7.34 (d, $J = 8.7$ Hz, 1 H, H(4), 6MQ), 7.08–6.70 (overlapping mult, 9 H total, H_p (OAr), H_m (OAr), and H(4), H(5) and H(7), 6MQ), 6.59 (dd, $J = 5.2$ and 8.7 Hz, 1 H, H(3), 6MQ), 4.46 and 3.76 (spt, 2 H each, C*H*Me_2), 1.55 (s, 3 H, CH_3, 6MQ), 1.03 and 0.64 (d, 12 H each, CH*Me*$_2$). ^{13}C NMR (C_6D_6): δ 158.3 and 157.5 (C_{ipso}, OAr), 141.0 and 140.9 (C_o, OAr), 126.0 and 125.5 (C_m, OAr), 124.2 (C_p, OAr), 155.3, 144.7, 137.1, 133.2, 129.9, 127.7, 126.5, 124.1, 120.4 (C(2) through C(10), 6MQ), 26.5 and 26.4 (*C*HMe_2), 24.8 and 24.6 (CH*Me*$_2$), 20.5 (CH_3, 6MQ). Calc. for $C_{34}H_{43}Cl_3$

NO_2Ta: C, 52.04; H, 5.48. Found: C, 51.90; H, 5.33.

[η^2(N,C)-QUIN]Ta(OAr)$_3$ (**5**). A solution of 4.50 g (4.93 mmol) of [η^1(*N*)-QUIN]Ta(OAr)$_3$Cl$_2$ (**1**) was prepared in diethyl ether (*ca* 40 cm^3) and cooled to −35°C. This cold solution was rapidly stirred while a large excess of NaHg (0.50%, 5.0 cm^3, 14.8 mmol Na) was added, whereupon the solution quickly turned bright orange in colour. Rapid stirring was continued while the mixture was warmed to room temperature and over time the solution developed a deep burgundy colour. After 4 h reaction time the burgundy solution was decanted from the amalgam layer, filtered through Celite, and the Celite was washed with diethyl ether (*ca* 40 cm^3) until the washings were colourless. The reaction volatiles were removed from the dark red filtrate *in vacuo* to provide a sticky, red–brown powder. This solid was dried under high vacuum (*ca* 10^{-4} torr) for 12 h to afford 3.21 g (3.82 mmol, 77%) of [η^2(*N*,*C*)-QUIN]Ta(OAr)$_3$ (**5**) as a red solid. Because of its *extreme* solubility as well as its thermal sensitivity, this compound has not been obtained completely pure, therefore elemental analyses have not been attempted. ^{1}H NMR (C_6D_6): δ 7.06–6.92 (A_2B mult, 9 H, H_{aryl}, OAr), 6.81 (dd, J = 3.5 and 5.6 Hz, 1 H, H(5), QUIN), 6.670 and 6.656 (overlapping d, J = 5.7 and 5.6 Hz, respectively, 1 H each, H(7) and H(8), QUIN), 6.46 (dd, J = 3.5 and ~5.6 Hz, 1 H, H(6), QUIN), 6.39 (dd, J = 9.4 and 1.2 Hz, 1 H, H(3), QUIN), 6.01 (d, J = 9.5 Hz, 1 H, H(4), QUIN), 4.07 (s, 1 H, H(2), QUIN), 3.50 (spt, 6 H, C*H*Me$_2$), 1.17 and 1.11 (d, 18 H each, CH*Me*$_2$). ^{13}C NMR (C_6D_6): δ 156.8 (C_{ipso}, OAr), 151.2 (C(9) or C(10), QUIN), 138.0 (C_o, OAr), 125.5 (C(10) or C(9), QUIN), 123.8 (C_p, OAr), 123.6 (C_m, OAr), 131.9, 127.2, 124.1, 123.4, 123.3, 122.9 (C(3), C(4), C(5), C(6), C(7), and C(8), QUIN), 76.4 (C(2), QUIN), 27.6 (*C*HMe$_2$, OAr), 23.9 and 23.7 (CH*Me*$_2$, OAr).

[η^2(N,C)-6MQ]Ta(OAr)$_3$ (**6**). A solution of 3.23 g (3.48 mmol) of [η^1(*N*)-6MQ]Ta(OAr)$_3$Cl$_2$ (**2**) was prepared in diethyl ether (*ca* 40 cm^3) and cooled to −35°C. This solution was stirred rapidly while a large excess of NaHg (0.50%, 3.55 cm^3, 10.5 mmol Na) was added: whereupon the solution quickly turned bright orange in colour. Rapid stirring was continued while the mixture was warmed to room temperature and over time the solution was observed to develop a burgundy colour. After 4 h the deep red solution was decanted from the amalgam, filtered through Celite, and the Celite was washed with diethyl ether (*ca* 40 cm^3) until the washings became colourless. The reaction volatiles were removed from the filtrate *in vacuo* to afford 2.10 g (2.45 mmol, 71%) of [η^2(*N*,*C*)-6MQ]Ta(OAr)$_3$ (**6**) as a red solid. Samples of **6** obtained in this manner were spectroscopically pure; however, the extreme thermal and air/moisture sensitivity of this compound made elemental analyses difficult. Compound **6** could be recrystallized from pentane solution at −35°C. ^{1}H NMR (C_6D_6): δ 7.06–6.92 (pseudo d and t (A_2B mult), 9 H total, H_{aryl}, OAr), 6.64 (s, 1 H, H(5), 6MQ), 6.50 (d, $J \approx 8$ Hz, 1 H, H(7) or H(8), 6MQ), 6.40 (d, J = 9.3 Hz, 1 H, H(3) or H(4), 6MQ), 6.38 (d, J = 7.9 Hz, 1 H, H(8) or H(7), 6MQ), 6.01 (d, J = 9.4 Hz, 1 H, H(4) or H(3), 6MQ), 4.11 (s, 1 H, H(2), 6MQ), 3.51 (spt, 6 H, C*H*Me$_2$), 2.11 (s, 3 H, CH_3, 6MQ), 1.18 and 1.12 (d, 18 H each, CH*Me*$_2$). ^{13}C NMR (C_6D_6): δ 156.8 (C_{ipso}, OAr), 149.0 (C(9) or C(10), 6MQ), 138.0 (C_o, OAr), 132.3 (C(6), 6MQ), 131.4, 127.7, 126.7 (C(5), C(7), and C(8), 6MQ), 125.30 (C(10) or C(9), 6MQ), 123.7 (C_p, OAr), 123.6 (C_m, OAr), 123.4 (C(3) or C(4), 6MQ), 122.7 (C(4) or C(3), 6MQ), 76.6 (C(2), 6MQ), 27.6 (*C*HMe$_2$), 23.9 and 23.7 (CH*Me*$_2$), 20.8 (CH_3, 6MQ). Calc. for $C_{46}H_{60}O_3NTa$: C, 64.55; H, 7.07; N, 1.64. Found: C, 65.90; H, 7.45; N, 1.50.

[η^2(N,C)-QUIN]Ta(OAr)$_3$(PMe$_3$) (**7**). (i) A 0.40 cm^3 (3.9 mmol) quantity of PMe$_3$ was added directly (neat) to a rapidly stirred solution of [η^2(*N*,*C*)-QUIN]Ta(OAr)$_3$ (**5**) (1.60 g, 1.90 mmol) in 15 cm^3 of pentane. This mixture was allowed to react for 14 h, over which time a burnt orange precipitate slowly formed. The reaction volatiles were removed *in vacuo* to afford a red–brown oil which was reconstituted with minimal pentane (*ca* 10 cm^3), whereupon the product formed as a burnt orange solid. This solid (0.71 g, 0.77 mmol) was filtered off and dried *in vacuo*. Cooling the dark red filtrate to −35°C provided an additional 0.21 g (0.25 mmol) of [η^2(*N*,*C*)-QUIN]Ta(OAr)$_3$(PMe$_3$) (**7**) for a total yield of 54%.

(ii) Extremely pure, highly crystalline **7** may also be obtained without isolation of [η^2(*N*,*C*)-QUIN]Ta(OAr)$_3$ (**5**) as follows. A solution of 4.500 g (4.93 mmol) [η^1(*N*)-QUIN]Ta(OAr)$_3$Cl$_2$ (**1**) was prepared in Et_2O (*ca* 40 cm^3) and cooled to −35°C. This cold solution was rapidly stirred while excess NaHg (0.50%, 3.6 cm^3, 10.6 mmol Na) was added. After being stirred for 4 h, the resultant dark red solution was decanted from the amalgam and filtered through Celite. The filtrate was then cooled to −78°C and excess PMe$_3$ (1.00 cm^3, 11.2 mmol) was condensed into the unstirred solution. Over the course of several hours, lovely orange crystals were seen to form. After 24 h, the deep red solution was decanted away and the remaining orange crystals were dried *in vacuo* to provide 1.311 g (1.43 mmol, 29%) of [η^2(*N*,*C*)-QUIN]Ta(OAr)$_3$(PMe$_3$) (**7**) as an analytically pure, orange crystalline solid. ^{1}H

NMR (C_6D_6): δ 7.03–6.68 (overlapping mult, 14 H total, H_{aryl}, OAr and H(8), H(7), H(6), H(5), and H(3) or H(4), QUIN), 6.26 (d, $J = 9.4$ Hz, 1 H, H(4) or H(3), QUIN), 3.62 (s, 1 H, H(2), QUIN), 3.36 (br, 6 H, C*H*Me_2), 1.08 (br s, 36 H, CH*Me*$_2$), 0.97 (d, $J = 6.7$ Hz, 9 H, PMe_3). ^{13}C NMR (C_6D_6): δ 157.2 (C_{ipso}, OAr), 150.6 (C(9) or C(10), QUIN), 137.8 (C_o, OAr), 133.1, 127.5, 126.6, 125.4, 124.5, 123.0 (C(8), C(7), C(6), C(5), C(4), and C(3), QUIN), 125.4 (C(10) or C(9), QUIN), 123.9 (C_m, OAr), 121.8 (C_p, OAr), 67.5 (C(2), QUIN), 26.7 (*C*HMe$_2$), 25.0 and 24.6 (CH*Me*$_2$), 13.6 (d, $J = 14.6$ Hz, PMe_3). Calc. for $C_{48}H_{67}O_3NPTa$: C, 62.80; H, 7.36; N, 1.53. Found: C, 62.79; H, 7.47; N, 1.61.

[η^2(N,C)-6MQ]Ta(OAr)$_3$(PMe_3) (**8**). A solution of 4.50 g (4.86 mmol) of [η^1(*N*)-6MQ]Ta(OAr)$_3$Cl$_2$ (**2**) in diethyl ether (*ca* 40 cm^3) was prepared and cooled to -35°C. This solution was rapidly stirred while excess NaHg (0.50%, 4.8 cm^3, 14.1 mmol Na) was added. After 20 h the resulting deep red solution was decanted from the amalgam, filtered through Celite, and the filtrate was stripped *in vacuo* to provide a red solid. This solid was dissolved in pentane (*ca* 50 cm^3), cooled to -78°C, and then rapidly stirred while excess PMe_3 (*ca* 2.0 cm^3, 22.5 mmol) was added. After several hours reaction time, orange solid was seen to form. After 18 h, the reaction volitiles were removed *in vacuo* and the resulting orange solid was collected, washed with pentane (*ca* 50 cm^3), and dried *in vacuo* to provide 1.895 g (2.03 mmol) of [η^2(*N*,*C*)-6MQ]Ta(OAr)$_3$(PMe_3) (**8**). An additional 0.895 g (0.96 mmol) of product was obtained by cooling the deep red filtrate to -35°C for a total yield of 61%. Analytically pure [η^2(*N*,*C*)-6MQ]Ta(OAr)$_3$(PMe_3) (**8**) may be obtained by recrystallization from pentane at -35°C. ^{1}H NMR (C_6D_6): δ 7.04–6.86 (A_2B mult, 9 H, H_{aryl}, OAr), 6.81 (d, $J = 1.3$ Hz, 1 H, H(5), 6MQ), 6.75 (dd, $J = 1.3$ and 9.3 Hz, 1 H, H(7), 6MQ), 6.72 (d, $J = 8.0$ Hz, 1 H, H(4), 6MQ), 6.51 (dd, 1 H, $J = 1.6$ and 8.0 Hz, H(3), 6MQ), 6.27 (d, 1 H, $J = 9.3$ Hz, H(8), 6MQ), 3.68 (br s, 1 H, H(2), 6MQ), 3.34 (br, 6 H, C*H*Me_2), 2.12 (s, 3 H, CH_3, 6MQ), 1.07 (br, 36 H, CH*Me*$_2$), 0.97 (d, $J_{PH} = 6.6$ Hz, PMe_3). ^{13}C NMR (C_6D_6): δ 157.2 (C_{ipso}, OAr), 148.3 (C(9), 6MQ), 137.8 (C_o, OAr), 133.1 (C(4), 6MQ), 132.0 (C(6), 6MQ), 128.2, 127.0, and 124.2 (C(5), C(7), and C(8), 6MQ), 125.2 (C(10), 6MQ), 123.9 (C_m, OAr), 121.7 (C_p, OAr), 67.4 ($^1J_{CH} = 156.4$ Hz, C(2), 6MQ), 26.6 (*C*HMe$_2$), 25.1 and 24.6 (CH*Me*$_2$), 20.8 (CH_3, 6MQ), 14.0 (d, PMe_3). One resonance for the 6MQ set C(3), C(5), C(7), and C(8) is not observed; we assign this unobserved signal as C(3), which is most likely obscured by solvent resonances or is coincident with the C_m (OAr) signal at δ 123.9. Calc. for $C_{48}H_{69}NO_3PTa$: C, 63.15; H, 7.46; N, 1.50. Found: C, 63.43; H, 7.77; N, 1.39.

[η^2(N,C)-6MQ]Ta(OAr)$_2$Cl(OEt$_2$) (**9**). (i) A solution of Ta(OAr)$_2$Cl$_3$(OEt$_2$) (1.50 g, 2.10 mmol) was prepared in 20 cm^3 of diethyl ether and cooled to -35°C. To this cold, rapidly stirred solution was added 6-methylquinoline (0.28 cm^3, 2.10 mmol) followed by excess NaHg (0.50%, 1.43 cm^3, 4.20 mmol Na). (*NOTE: Although this preparation afforded crystals of* **9**, *more reproducible results were obtained using* 4 *equiv. of* NaHg.) Upon amalgam addition the solution colour rapidly changed from bright yellow to green. The reaction mixture was then shaken vigorously for 5 min, over which time it gradually became brown in colour. This brown solution was decanted from the amalgam and filtered through Celite and the filtrate was stripped to dryness *in vacuo*. The resulting brown solid was dissolved in diethyl ether (*ca* 20 cm^3) and stored at -35°C for one week, over which time a red solid had precipitated. This solid was collected by filtration and dried *in vacuo* to provide 0.751 g (0.953 mmol, 45%) of [η^2(*N*,*C*)-6MQ]Ta(OAr)$_2$Cl(OEt$_2$) (**9**). Complex **9** made by this route is invariably contaminated with what appears to be paramagnetic [η^1(*N*)-6MQ]$_2$Ta(OAr)$_2$Cl$_2$ (**11**), which is virtually impossible to separate from **9**.

(ii) A solution of (η^6-C_6Me_6)Ta(OAr)$_2$Cl (1.00 g, 1.36 mmol) was prepared in pentane/diethyl ether (90 cm^3/10 cm^3) and was cooled to -70°C. To this rapidly stirred solution was added a solution of 6-methylquinoline (0.40 cm^3, 2.70 mmol) in diethyl ether (20 cm^3), which had also been cooled to -70°C. This mixture was allowed to warm slowly to room temperature over the course of 18 h. The orange flocculent precipitate which had formed was collected on a frit, washed with cold pentane (*ca* 40 cm^3) to remove free C_6Me_6, and dried *in vacuo* to afford 0.987 g (1.25 mmol, 91.9%) of [η^2(*N*,*C*)-6MQ]Ta(OAr)$_2$Cl(OEt$_2$) (**9**) as a light orange solid. ^{1}H NMR (C_6D_6): δ 9.46 (d, $J = 5.0$ Hz, 1 H, H(5), 6MQ), 7.46 (d, $J = 8.5$ Hz, 1 H, H(8), 6MQ), 7.03–6.89 (broad overlapping signals, 6 H, H_{aryl}, OAr), 6.72 and 6.05 (br s and d ($J = 9.0$ Hz), 1 H each, H(3) and H(4), 6MQ), 6.56 (dd, $J = 5.0$ and 8.5 Hz, 1 H, H(7), 6MQ), 4.69 (br s, 1 H, H(2), 6MQ), 3.49 (br, 4 H, C*H*Me_2), 3.26 (q, 4 H, CH_2, Et_2O), 1.81 (s, 3 H, CH_3, 6MQ), 1.21 (two d overlapping with t, 30 H total, CH*Me*$_2$ and CH_3, OEt$_2$). The rapid thermal decomposition of this complex has prevented the acquisition of reliable ^{13}C NMR data. Calc. for $C_{38}H_{53}ClNO_3Ta$: C, 57.90; H, 6.78; Cl, 4.50; N, 1.78. Found: C, 57.20; H, 6.71; Cl, 4.66; N, 1.65.

[η^1(*N*)-QUIN]$_2$Ta(OAr)$_2$Cl$_2$ (**10**). A solution of Ta(OAr)$_2$Cl$_3$(OEt$_2$) (1.50 g, 2.10 mmol) was pre-

pared in 20 cm^3 of diethyl ether and cooled to $-35°C$. This cold solution was rapidly stirred while 2 equiv. of quinoline (0.495 cm^3, 4.20 mmol), followed by 1 equiv. of NaHg (0.50%, 0.712 cm^3, 2.10 mmol Na), were added. The mixture rapidly turned dark green upon adding the amalgam. This reaction mixture was then shaken vigorously for 5 min, after which the dark green solution was decanted from the amalgam and filtered through Celite. The Celite was washed with diethyl ether (*ca* 25 cm^3) until the washings were colourless. Removing the reaction volatiles *in vacuo* afforded 1.13 g (1.31 mmol, 62%) of product as a forest green solid. Samples of $[\eta^1(N)\text{-QUIN}]_2Ta(OAr)_2Cl_2$ (**10**) obtained in this manner were analytically pure. ESR (room temperature, toluene solution): $g_{avg} = 1.82$; $A(^{181}Ta) = 222$ G. Cyclic voltammetry (0.1 M *n*-Bu_4NPF_6 in THF): $E_{pa} = 0.452$ V vs Ag/AgCl. IR (Et_2O solution): 1512 m, 1480 m, 1466 m, 1437 m, 1331 m, 1256 m-s, 1202 m, 1140 vs, 1136 s, 1132 s, 1113 s, 899 m, 878 w, 806 w, 779 w, 750 w, 710 w, 596 w cm^{-1}. Calc. for $C_{42}H_{48}Cl_2N_2O_2Ta$: C, 58.34; H, 5.60; N, 3.24. Found: C, 58.42; H, 6.19; N, 3.32.

$[\eta^1(N)\text{-6MQ}]_2Ta(OAr)_2Cl_2$ (**11**). A solution of $Ta(OAr)_2Cl_3(OEt_2)$ (1.50 g, 2.10 mmol) was prepared in 20 cm^3 of diethyl ether and cooled to $-35°C$. To this cold, rapidly stirred solution was added 6-methylquinoline (0.575 cm^3, 4.20 mmol) followed by NaHg (0.50%, 0.712 cm^3, 2.10 mmol Na). Upon amalgam addition the solution colour rapidly changed from bright yellow to dark green. The reaction mixture was then shaken vigorously for 5 min, after which the dark green solution was decanted from the amalgam and filtered through Celite. The Celite was washed with diethyl ether (*ca* 25 cm^3) until the washings were colourless. The reaction volatiles were removed from the filtrate *in vacuo* to provide 1.25 g (1.40 mmol, 67%) of product as a forest green solid. Samples of $[\eta^1(N)\text{-6MQ}]_2Ta(OAr)_2Cl_2$ (**11**) obtained in this manner were analytically pure. ESR (room temperature, toluene solution): $g_{avg} = 1.82$; $A(^{181}Ta) = 222$ G. Cyclic voltammetry (0.1 M *n*-Bu_4NPF_6 in THF): $E_{pa} = 0.432$ V vs Ag/AgCl. IR (Et_2O solution): 2359 m-w, 1508 m, 1464 m-w, 1437 s, 1333 s, 1256 s, 1202 s, 1140 s, 1111 m, 899 s, 878 m, 824 m-w, 750 m, 708 m-w cm^{-1}. Calc. for $C_{44}H_{52}Cl_2N_2O_2Ta$: C, 59.20; H, 5.87; N, 3.14. Found: C, 58.33; H, 6.54; N, 2.78.

$[\eta^1(N)\text{-py}]_2Ta(OAr)_2Cl_2$ (**12**). A solution of $Ta(OAr)_2Cl_3(OEt_2)$ (0.863 g, 1.21 mmol) and pyridine (0.200 cm^3, 2.47 mmol) was prepared in 15 cm^3 of diethyl ether and was cooled to *ca* $-78°C$ in an isopropanol/dry ice bath. To this solution was added NaHg (1 cm^3, 0.5% Na, 2.96 mmol) and the mixture was vigorously shaken for 10 min. Over this time the solution colour slowly changed from yellow to blue and finally to dark purple. This mixture was allowed to warm to room temperature and was filtered through Celite. The filtrate was stripped to dryness *in vacuo* to yield 0.866 g (1.13 mmol, 94%) of product as an intensely coloured, purple solid. Analytically pure $[\eta^1(N)\text{-py}]_2Ta(OAr)_2Cl_2$ (**12**) may be obtained by recrystallization from Et_2O at $-35°C$. ESR (room temperature, benzene solution): $g_{avg} = 1.81$; $A(^{181}Ta) = 228$ G. Cyclic voltammetry (0.1 M *n*-Bu_4NPF_6 in THF): $E_{pa} = 0.449$, $E_{pc} = -1.247$ V vs Ag/AgCl. IR (Et_2O solution): 2359 m-w, 1485 w, 1464 w, 1437 m, 1333 s, 1258 s, 1202 s, 1159 m, 1156 m, 1140 vs, 1129 vs, 1117 m, 1104 m, 899 s, 878 w, 751 w, 708 w, 693 w, 596 w cm^{-1}. Mass spectrum (EI, 70 eV): 762.2 (M^+) 15%, 605.1 ($M^+ - 2$ Py), 100%. Calc. for $C_{34}H_{44}Cl_2N_2O_2Ta$: C, 53.41; H, 5.80; N, 3.66; Cl, 9.27. Found: C, 54.57; H, 6.16; N, 3.96; Cl, 8.69.

X-ray structural determinations

Table 2 summarizes the crystal data and collection, solution and refinement parameters for both $[\eta^2(N,C)\text{-6MQ}]Ta(OAr)_3(PMe_3)$ (**8**) and $[\eta^2(N,C)\text{-6MQ}]Ta(OAr)_2Cl(OEt_2)$ (**9**). Hydrogen atoms were placed in calculated positions and included in the refinement.

Structural studies of $[\eta^2(N,C)\text{-6MQ}]Ta(OAr)_3(PMe_3)$ (**8**)

A yellow rectangular block crystal of **8** was crystallized from heptane/toluene solution ($-35°C$) and was mounted in a glass capillary in a random orientation. From the systematic absences *hkl*, $h+k = 2n+1$; *h*0*l*, $l = 2n+1$; and 0*k*0, $k = 2n+1$; and from subsequent least-squares refinement, the space group was determined to be $C2_1/c$ (No. 15). Three reflections were rejected from the averaging process because their intensities differed significantly from the average.

Structural studies of $[\eta^2(N,C)\text{-6MQ}]Ta(OAr)_2Cl(Et_2O)$ (**9**)

A red irregular crystal of **9** was obtained from the Et_2O reaction solution (from the reduction preparation) which had been filtered, concentrated *in vacuo*, and cooled to $-35°C$. This crystal was mounted in a glass capillary in a random orientation. From the systematic absences of *h*0*l*, $h+l = 2n+1$; 0*k*0, $k = 2n+1$ and from subsequent least-squares refinement, the space group was determined to be $P2_1/n$ (No. 14). The crystal decayed

during data collection with a total loss in intensity of 18%. The ethyl groups of the Et_2O molecule were disordered; this disorder was modelled as two sets of 1/2 occupancy side-chains. The highest peak in the final difference Fourier was located within 0.2 Å of the Ta atom and the second highest peak (0.54 e^- $Å^{-3}$) was located near the disordered Et_2O groups.

Hydrogenation study of [η^2(N,C)-QUIN]Ta(OAr)$_3$

In the dry box, a Fischer–Porter reactor was charged with a solution of [η^2(*N,C*)-QUIN]Ta(OAr)$_3$ (**5**, 0.97 g, 1.15 mmol) in 40 cm^3 of diethyl ether. The reaction vessel was pressurized with H_2 to 125 psi and the dark red solution was stirred at this pressure for exactly 24 h. After this time the pressure was vented and the resulting light red solution was transferred to a round bottomed flask, sealed with a rubber septum, and removed to the Schlenk line. To this solution was added excess water (5 cm^3, 0.277 mol), which led to a rapid bleaching of the solution and the formation of a flocculent white solid (presumably hydrous Ta_2O_5). After stirring this mixture for 1 h, the solution was filtered through Celite. The ether layer of the filtrate was decanted and the water layer was extracted with additional diethyl ether (3 × 20 cm^3). The ether layers were combined, dried with $MgSO_4$ (*ca* 1 g) and concentrated to exactly 10.0 cm^3. The sample was stored at −15°C until analysis by GC-MS.

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