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Tantalum Amido and Imido Complexes Supported by *Tris*[(2-indolyl)methyl]amine, a Tetradentate Trianionic Ligand with Reduced π-Donor Character

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Tris[(2-indole)methyl]amine, $N(CH_2inH)_3$, may be readily obtained by reaction of methyl 2-bromomethyl-1-indolecarboxylate with NH_3 followed by deprotection with NaOMe/MeOH. In its deprotonated form, $[N(CH_2in)_3]^{3-}$ is an efficient tetradentate trianionic ligand for tantalum, as illustrated by the isolation and structural characterization of $[\eta^4\text{-}N(CH_2in)_3]Ta(NAr)(NMe_2H)$ (Ar = 2,6-$C_6H_3Pr^i_2$), $[\eta^4\text{-}N(CH_2in)_3]Ta(NMe_2)_2$ and $[\eta^4\text{-}N(CH_2in)_3]Ta(NMe_2)Cl$. The $[N(CH_2in)_3]^{3-}$ ligand has a structural similarity to that of $[N(CH_2CH_2NR)_3]^{3-}$, but differs electronically from the latter due to its reduced π-donor capability, a direct result of the nitrogen being a component of the aromatic π-system of the indolyl fragment.

C_3 symmetric tridentate tripodal ligands are a prominent feature of modern coordination chemistry and collectively stabilize a diverse array of metal ligand combinations. The ability of tripodal ligands to achieve such diversity is in part a consequence of the fact that these ligands vary from neutral (L_3) to trianionic (X_3) donors.[1,2] In addition to tridentate tripodal ligands, *tetra*dentate tripodal ligands are also known, in which the extra donor functionality is provided by the axial linker atom, most commonly nitrogen.[3] A particularly interesting class of such ligand is one which is trianionic (LX_3) and features amido donors, namely tris(amidoethyl)amine and its various derivatives, *i.e.* $[N(CH_2CH_2NR)_3]^{3-}$.[4,5] For example, Schrock has extensively applied this class of ligand to a study of the chemistry of the early transition metals.[6] In large part, the success of the $[N(CH_2CH_2NR)_3]^{3-}$ ligand system in stabilizing high oxidation state compounds is associated with the well-known strongly π-donating properties of the amido functionality.[7,8] Modulation of both structure and reactivity is to be expected if the π-donor properties of the ligand were to be either reduced or eliminated. In this paper, we report the synthesis of a tetradentate trianionic donor ligand in which the π-donor properties of the nitrogen atom are reduced compared to that of an alkylamido functionality.

Recent studies have noted that aromatic cyclic counterparts to R_2N, such as pyrrolyl, indolyl, and carbazolyl exhibit a reduced π-donor capability as a result of the nitrogen π-orbital being involved in the aromatic π-system.[9] Therefore, in an effort to obtain tetradentate tripodal nitrogen ligands for which the π-donor properties are reduced from that of the $[N(CH_2CH_2NR)_3]^{3-}$ class, we sought to synthesize derivatives in which the nitrogen atom donors are components of heterocyclic rings. A clear indication that delocalization of the electron density on nitrogen may have a profound effect on the electron donating properties of such ligands is illustrated by the pK_a's of some simple derivatives: thus, the pK_a's of pyrrole (17.5), indole (17.0) and carbazole (16.5)[10] are significantly lower than those of simple amines, *e.g.* Pr^i_2NH (35.7),[11] $(Me_3Si)_2NH$ (29.5),[11] and Ph_2NH (22.4).[12] In addition to modulating the donor property of the ligand, another reason for using heterocyclic donors is that it should prevent so-called "cage decomposition" reactions of $[N(CH_2CH_2NR)_3]^{3-}$ which involve cleavage of

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(1) Common examples of tripod nitrogen donors include neutral *tris*(pyrazolyl)methane and *tris*(pyridyl)methane, monoanionic *tris*(pyrazolyl)hydroborato, and trianionic *tris*[(amido)methyl]ethane. See, for example: Gade, L. H. *Acc. Chem. Res.* **2002**, *35*, 575−582.

(2) For the $[L_lX_x]$ classification of ligands, see: Green, M. L. H. *J. Organomet. Chem.* **1995**, *500*, 127−148.

(3) For an example of a tetradentate tripodal ligand in which B−H is the axial donor, see: Bridgewater, B. M.; Parkin, G. *Inorg. Chem. Commun.* **2000**, *3*, 534−536.

(4) (a) Verkade, J. G. *Acc. Chem. Res.* **1993**, *26*, 483−489. (b) Verkade, J. G. *Coord. Chem. Rev.* **1994**, *137*, 233−295.

(5) Tetradentate tetraanionic ligands are also known. See: Kobayashi, J.; Goto, K.; Kawashima, T.; Schmidt, M. W.; Nagase, S. *J. Am. Chem. Soc.* **2002**, *124*, 3703−3712.

(6) (a) Schrock, R. R. *Acc. Chem. Res.* **1997**, *30*, 9−16. (b) Schrock, R. R. *Pure Appl. Chem.* **1997**, *69*, 2197−2203.

(7) Bradley, D. C.; Chisholm, M. H. *Acc. Chem. Res.* **1976**, *9*, 273−280.

(8) Cummins, C. C. *Prog. Inorg. Chem.* **1998**, *47*, 685−836.

(9) See, for example: (a) Riley, P. N.; Parker, J. R.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1999**, *18*, 3579−3583. (b) Riley, P. N.; Fanwick, P. E.; Rothwell, I. P. *J. Chem. Soc., Dalton Trans.* **2001**, 181−186. (c) Harris, S. A.; Ciszewski, J. T.; Odom, A. L. *Inorg. Chem.* **2001**, *40*, 1987−1988. (d) Tanski, J. M.; Parkin, G. *Organometallics* **2002**, *21*, 587−589. (e) Zhu, G.; Tanski, J. M.; Parkin, G. *J. Chem. Crystallogr.* **2002**, *32*, 461−467.

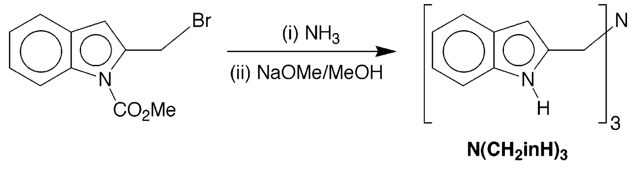
(10) Catalan, J.; Abboud, J. L. M.; Elguero, J. *Adv. Heterocycl. Chem.* **1987**, *41*, 187−274.

(11) Fraser, R. R.; Mansour, T. S. *J. Org. Chem.* **1984**, *49*, 3442−3443.

(12) Stewart, R.; Dolman, D. *Can. J. Chem.* **1967**, *45*, 925−928.

10.1021/ic026182a CCC: $25.00

Scheme 1



one of the N−CH_2CH_2NR bonds and the formation of a vinyl amide fragment, CH_2═CHNR.[13]

Focusing first on the incorporation of the indolyl fragment, we have found that *tris*[(2-indole)methyl]amine, $N(CH_2inH)_3$, may be readily obtained by reaction of methyl 2-bromomethyl-1-indolecarboxylate[14] with NH_3, followed by deprotection with NaOMe/MeOH (Scheme 1).[15] $N(CH_2inH)_3$ has been characterized spectroscopically and by an X-ray diffraction study on the protected form, $N(CH_2inCO_2Me)_3$.[16] The structure of $N(CH_2inH)_3$ is closely related to that of *tris*-[(2-benzimidazolyl)methyl]amine, $N(CH_2bimH)_3$,[17,18] differing merely in the formal substitution of a CH group by N in the 5-membered heterocyclic ring. Despite the structural similarity, however, the two molecules are electronically quite distinct because $N(CH_2inH)_3$ can only operate as a tetradentate ligand once it has been triply deprotonated, *i.e.* $[N(CH_2in)_3]^{3-}$, whereas $N(CH_2bimH)_3$ may operate as a tetradentate ligand in its *neutral* form. The ability of the latter to act as a neutral donor is merely a consequence of the fact that the 5-membered imidazolyl ring already has a two-coordinate nitrogen that may function as a donor. In principle, deprotonation of $N(CH_2bimH)_3$ would enable it to act as an anionic ligand, but the deprotonated nitrogen would undoubtedly be a site of subsequent reactivity and thereby render the ligand non-innocent; deprotonated $N(CH_2bimH)_3$ has thus found little application as a ligand to date.[19]

Another feature of $N(CH_2bimH)_3$ that hinders its application to early transition metal chemistry is its insolubility in inert solvents. Indeed, transition metal derivatives of $N(CH_2bimH)_3$ are mainly limited to those of the later metals[20] and are commonly obtained by reactions that employ alcohols as solvents. In contrast, $N(CH_2inH)_3$ is soluble in benzene, thereby facilitating the synthesis of derivatives of the early transition metals, as specifically described here for tantalum.

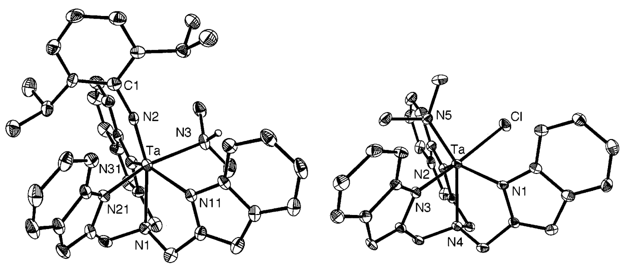
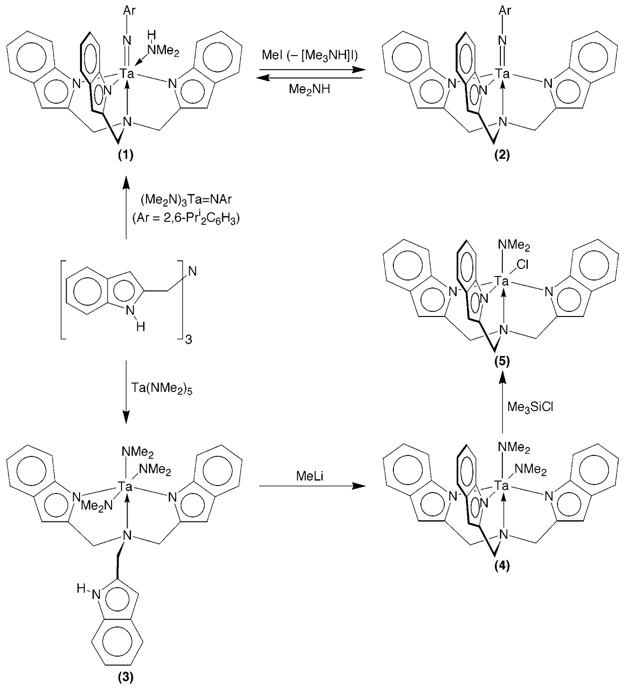


Figure 1. Molecular structures of [η^4-$N(CH_2in)_3$]Ta(NAr)(NMe_2H) (**1**) and [η^4-$N(CH_2in)_3$]Ta(NMe_2)Cl (**5**).

Scheme 2



The synthesis of $[N(CH_2in)_3]$−tantalum derivatives may be achieved by the reactions of $N(CH_2inH)_3$ with dimethylamido tantalum complexes, reactions that are accompanied by elimination of Me_2NH. For example, $N(CH_2inH)_3$ reacts with $(Me_2N)_3Ta(NAr)$ (Ar = 2,6-$C_6H_3Pr^i{}_2$)[21] at room temperature to give the arylimido complex [η^4-$N(CH_2in)_3$]Ta-(NAr)(NMe_2H) (**1**), as illustrated in Scheme 2. The molecular structure of [η^4-$N(CH_2in)_3$]Ta(NAr)(NMe_2H) has been determined by X-ray diffraction (Figure 1)[16] and illustrates several important features. Firstly, the six Ta−N bond lengths of the distorted octahedral $[TaN_6]$ entity span the substantial range of 1.78−2.38 Å, varying according to the nature of the different donors which fall into three categories: (*i*) $Ta{=}N_{imido}$ double bond [1.778(6) Å], (*ii*) $Ta{-}N_{indolyl}$ single bond [2.11(2) Å (av)], and (*iii*) Ta←N dative bond, *i.e.* $Ta{\leftarrow}NR_3$ [2.380(5) Å] and $Ta{\leftarrow}NMe_2H$ [2.344(5) Å]. Secondly, the average $Ta{-}N_{indolyl}$ bond length of 2.11(2) Å is distinctly longer than the $Ta{-}N_{amido}$ bond lengths in

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(13) See, for example: (a) Freundlich, J. S.; Schrock, R. R.; Davies, W. M. *J. Am. Chem. Soc.* **1996**, *118*, 3643−3655. (b) Freundlich, J. S.; Schrock, R. R.; Davies, W. M. *Organometallics* **1996**, *15*, 2777−2783.

(14) Nagarathnam, D. *Synthesis* **1992**, 743−745.

(15) For a related example of the synthesis of a *tris*[(2-pyrrolyl)methyl]-amine, see: Treibs, A.; Jacob, K. *Liebigs Ann. Chem.* **1970**, *737*, 176−178.

(16) See Supporting Information.

(17) See, for example: (a) Thompson, L. K.; Ramaswamy, B. S.; Seymour, E. A. *Can. J. Chem.* **1977**, *55*, 878−888. (b) Oki, A. R.; Bommarreddy, P. R.; Zhang, H.; Hosmane, N. *Inorg. Chim. Acta* **1995**, *231*, 109−114. (c) Su, C.-H.; Kang, B.-S.; Du, C.-X.; Yang, Q.-C.; Mak, T. C. W. *Inorg. Chem.* **2000**, *39*, 4843−4849.

(18) Alkylated derivatives, $N(CH_2bimR)_3$, are also known. See, for example: (a) Reference 17c. (b) Hendriks, H. M. J.; Birker, P.; Verschoor, G. C.; Reedijk, J. *J. Chem. Soc., Dalton Trans.* **1982**, 623−631.

(19) We are aware of one example where a coordinated $N(CH_2bimH)_3$ ligand has been triply deprotonated, namely $\{[N(CH_2bimH)_3]Co(NCS)\}^+$; the deprotonated nitrogen atoms are, however, readily reprotonated, thereby indicating the non-innocent nature of the deprotonated ligand. See: Hammes, B. S.; Kieber-Emmons, M. T.; Sommer, R.; Rheingold, A. L. *Inorg. Chem.* **2002**, *41*, 1351−1353.

(20) For example, there are no structurally characterized $N(CH_2bimH)_3$ derivatives of the groups 4 and 5 transition metals listed in the Cambridge Structural Database (Version 5.23).

(21) Hermann, W. A.; Baratta, W.; Herdtweck, E. *J. Organomet. Chem.* **1997**, *541*, 445−460.

{[N(CH_2CH_2NR)$_3$]Ta} derivatives. For example, the mean Ta−N_{amido} bond length in structurally characterized {[N(CH_2CH_2NR)$_3$]Ta} derivatives listed in the Cambridge Structural Database is 2.02(3) Å, *ca*. 0.1 Å shorter than the average Ta−$N_{indolyl}$ bond length of [η^4-N(CH_2in)$_3$]Ta(NAr)(NMe_2H). The mean Ta−N_{amine} bond length [2.36(6) Å] for {[N(CH_2CH_2NR)$_3$]Ta} derivatives, however, is comparable to that for [η^4-N(CH_2in)$_3$]Ta(NAr)(NMe_2H) [2.380(5) Å], indicating that the difference in Ta−$N_{indolyl}$ and Ta−N_{amido} bond lengths is a manifestation of the different π-donor abilities of the nitrogen donors. Thirdly, the [N(CH_2in)$_3$]$^{3-}$ ligand is flexible and the local coordination geometry may deviate substantially from C_3 symmetry. For example, the N−Ta−N bond angles between the indolyl donors are quite disparate, with values of 86.9(2)°, 110.1(2)°, and 137.3(2)°.

Dissociation of Me_2NH from [η^4-N(CH_2in)$_3$]Ta(NAr)(NMe_2H) generates 5-coordinate [η^4-N(CH_2in)$_3$]Ta(NAr) (**2**). However, the dissociation is reversible, such that isolation of [N(CH_2in)$_3$]Ta(NAr) requires removal of the liberated Me_2NH, which may be achieved by treatment with MeI (Scheme 2).[22] The isolation of [η^4-N(CH_2in)$_3$]Ta(NAr)(NMe_2H) is also noteworthy in that it is stable with respect to proton transfer from the Me_2NH ligand to the arylimido ligand that would thereby form [N(CH_2in)$_3$]Ta(HNAr)(NMe_2). This observation is consistent with the notion that the nitrogen lone pair interacts strongly with the electron deficient tantalum center, thereby rendering the nitrogen unsusceptible to protonation.[23,24]

Coordination of the *tris*[(2-indolyl)methyl]amine ligand to tantalum may also be achieved by a two step sequence that involves the initial reaction of Ta(NMe_2)$_5$[9a,25] with N(CH_2inH)$_3$ at 70 °C to give [η^3-N(CH_2in)$_2$(CH_2inH)]Ta(NMe_2)$_3$ (**3**) (Scheme 2). The latter complex, which has been structurally characterized by X-ray diffraction (Figure 2), features a tridentate [η^3-N(CH_2in)$_2$(CH_2inH)]$^{2-}$ ligand in which only two of the indolyl donors coordinate to tantalum, with the uncoordinated indole fragment remaining protonated.

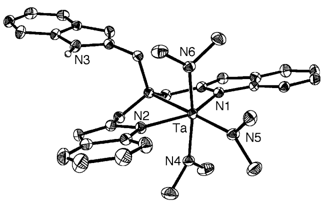

Figure 2. Molecular structure of [η^3-N(CH_2in)$_2$(CH_2inH)]Ta(NMe_2)$_3$ (**3**).

Coordination of the third indolyl group may be achieved by deprotonation with MeLi to give [η^4-N(CH_2in)$_3$]Ta(NMe_2)$_2$ (**4**) (Scheme 2). The molecular structure of [η^4-N(CH_2in)$_3$]Ta(NMe_2)$_2$ has been determined by X-ray diffraction, demonstrating that the structure may be described as distorted octahedral with *cis* NMe_2 ligands. The Ta−$N_{indolyl}$ bonds [2.13(2) Å (av)] are longer than those of the Ta−NMe_2 bonds [1.95(5) Å (av)], thereby providing a further demonstration that indolyl nitrogen atoms are poorer donors than the planar amide nitrogen atoms.

[η^4-N(CH_2in)$_3$]Ta(NMe_2)$_2$ reacts with Me_3SiCl to yield [η^4-N(CH_2in)$_3$]Ta(NMe_2)Cl (**5**). The molecular structure of [η^4-N(CH_2in)$_3$]Ta(NMe_2)Cl has been determined by X-ray diffraction, as illustrated in Figure 1,[26] and demonstrates that the Ta−$N_{indolyl}$ bond [2.08(3) Å (av)] is also longer than the Ta−NMe_2 [1.941(5) Å] bond in this complex.

In summary, [N(CH_2in)$_3$]$^{3-}$ has been shown to be an efficient tetradentate trianionic ligand for tantalum. In this regard, while the [N(CH_2in)$_3$]$^{3-}$ ligand has a structural similarity to that of [N(CH_2CH_2NR)$_3$]$^{3-}$, it differs electronically from the latter due to its reduced π-donor capability, which is a direct result of the nitrogen being a component of the aromatic π-system of the indolyl fragment. Furthermore, the trianionic nature of [N(CH_2in)$_3$]$^{3-}$ ligand promises access to a fundamentally different class of chemistry than that provided by its neutral isosteric benzimidazole counterparts, N(CH_2bimH)$_3$ and N(CH_2bimR)$_3$, as illustrated by the tantalum complexes reported here.

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Supporting Information Available: Experimental details (pdf) and crystallographic CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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(22) The interconversion of [η^4-N(CH_2in)$_3$]Ta(NAr)(NMe_2H) and [η^4-N(CH_2in)$_3$]Ta(NAr) is also rapid on the NMR time-scale, as indicated by ^{1}H NMR spectroscopy.

(23) Cundari, T. R. *J. Am. Chem. Soc.* **1992**, *114*, 7879−7888.

(24) In this regard, it is also worth noting that other dimethylamine−imido complexes are known, *e.g.* [$Me_2C(C_5H_4)_2M(NAr)(NMe_2H)$]$^+$ (M = Nb, Ta; Ar = 2,6-$C_6H_3Pr^i{}_2$)[a] and (ArO)$_3$Nb(NMe)(NMe_2H) (Ar = 2,6-$C_6H_3Ph_2$).[b] Furthermore, the relative inertness of many linear Ta═NR linkages has been noted.[c] (a) Reference 21. (b) Chesnut, R. W.; Fanwick, P. E.; Rothwell, I. P. *Inorg. Chem.* **1988**, *27*, 752−754. (c) Pugh, S. M.; Trösch, D. J. M.; Skinner, M. E. G.; Gade, L. H.; Mountford, P. *Organometallics* **2001**, *20*, 3531−3542.

(25) Bradley, D. C.; Thomas, I. M. *Can. J. Chem.* **1962**, *40*, 1355−1360.

(26) The iodide complex [η^4-N(CH_2in)$_3$]Ta(NMe_2)I has also been structurally characterized.