Another Surprise from Pyrazolate Ligands**

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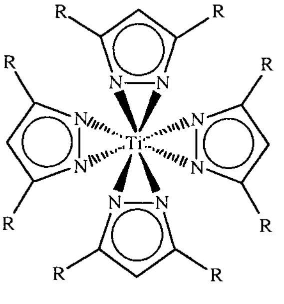
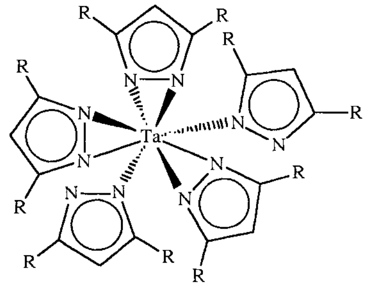
Winter et al.[1] recently synthesized two pyrazolatotitanium(IV) complexes [Ti(η^2-R$_2$pz)$_4$] (**1**, pz = pyrazolate, R = Ph, Me) with four 3,5-disubstituted pyrazolate rings. These are the first homoleptic pyrazolato complexes, and contain exclusively η^2-pyrazolate ligands. This was followed by the synthesis of the homoleptic 3,5-disubstituted pyrazolatotantalum(V) complex [Ta(η^2-Me$_2$pz)$_3$(η^1-Me$_2$pz)$_2$][2] (**2**), which has both η^1- and η^2-pyrazolate ligands. These complexes establish η^2-pyrazolate binding as a new feature in the chemistry of d-block transition metals. There is only one previous example of η^2-binding to a d-block element: [ZrCp$_2$(η^2-pz)(thf)](BPh$_4$) · 0.5 thf,[3] in which there is just one ligand of this type. The preparation of homoleptic pyrazolato complexes and in particular homoleptic (η^2-pyrazolato)titanium(IV) complexes is the most significant development in the coordination chemistry of these ligands since the unexpected discovery of *endo* bidentate (η^2) coordination in [UCp$_3$(η^2-pz)].[4] The bonding in [Ti(η^2-R$_2$pz)$_4$] contrasts the expected d-block bridging bidentate coordination seen in [{TiCp$_2$(μ-pz)}$_2$].[5] The homoleptic complexes **1** and **2** are of considerable interest as molecular precursors for chemical vapor deposition (CVD).[1, 2]

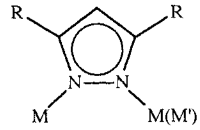


1

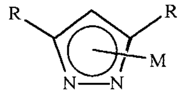


2

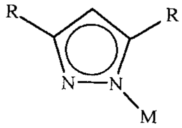
In his seminal review of pyrazole and pyrazolate coordination, Trofimenko considered two possible types of bonding for the pyrazolate ion: bridging [that is, *exo*-bidentate (**I**)] or η^5 (the pyrazolate functions as 1,2-diazacyclopentadienide).[6] However, claims of π bonding were dismissed as unsubstantiated,[6] and this mode of coordination (**II**) remains to be established. Unidentate coordination as in **III**, which is formally present in pyrazolylborates [R$_n$B(pz)$_{4-n}$]$^-$,[6, 7] was first crystallographically observed for bis[3-phenyl-5-(2′-pyridyl)pyrazolato]nickel(II).[8] In this case the coordination of the 2′-pyridyl nitrogen atom forces the metal to comply with unidentate rather than *exo* bidentate coordination. More latterly, several complexes with η^1-pyrazolate ligands have been prepared. In these cases unidentate coordination is generally dictated by the metal: Either only certain coordination sites are available, as in *cis*-chloro(η^1-3,5-diphenylpyrazolato)bis(triphenylphosphane)platinum(II),[9] or there are electronic requirements, as in bis(η^5-cyclopentadienyl)bis(η^1-pyrazolato)molybdenum(IV)[10] or [Me$_2$Ga(pz)$_2$]$^-$.[11]



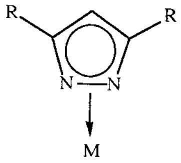
I



II



III



IV

The first observation of η^2-coordinated pyrazolate ligands (complexes of type **IV**) in [UCp$_3$(η^2-pz)] was unexpected; the authors anticipated [UCp$_3$(μ-pz)]$_2$.[4] This form of binding to an f-block metal was rationalized in terms of the highly ionic, nondirectional nature of the U–N bonds and binding to the more negative side of the pyrazolate ring. Other examples of η^2-coordinated pyrazolate ligands followed for uranium[12] and then for lanthanoids. This coordination mode was initially observed together with μ-pyrazolate binding.[13, 14] In an important subsequent development the first tris(η^2-pyrazolato)lanthanoid complexes [Ln(R$_2$pz)$_3$(L)$_n$] (L = thf, dme, Ph$_3$PO) were prepared by using the bulky 3,5-diphenyl- and 3,5-di-*tert*-butylpyrazolate ligands.[15] These were the first complexes with η^2-pyrazolates as the sole anionic ligands. These studies also introduced metal-based redox transmetalation/ligand exchange [Eq. (a); R = *t*Bu, Ph, R′ = C$_6$F$_5$] as a synthetic method, in contrast to the commonly used metatheses or deprotonations.[6, 7] However, the ligands were not bulky enough to produce homoleptic η^2-pyrazolato complexes for the large Ln^{3+} ions, but have now proven sufficiently bulky to give such complexes for the smaller (by ca. 15%)[16] titanium(IV).[1]

$$2\,\mathrm{Ln} + 6\,\mathrm{R_2pzH} + \mathrm{HgR'_2} \longrightarrow 2\,[\mathrm{Ln(R_2pz)_3}] + 3\,\mathrm{Hg} + 6\,\mathrm{R'H} \tag{a}$$

The failure to observe d-block transition metal complexes of η^2-coordinated pyrazolato ligands prior to [ZrCp$_2$(η^2-pz)(thf)](BPh$_4$)[3] was attributed to a correlation between common *exo* bidentate binding and the directional properties of the nitrogen donor atoms.[4, 6, 15] Even the example of [ZrCp$_2$(η^2-pz)(thf)](BPh$_4$), in contrast to the numerous

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d-block transition metal complexes of μ-pyrazolate ligands,[6, 7] can be viewed as an exceptional result of the need to achieve electronic saturation (18 electrons).

The syntheses of $[Ti(\eta^2\text{-}R_2pz)_4]$[1] and $[Ta(\eta^2\text{-}R_2pz)_3(\eta^1\text{-}R_2pz)_2]$[2] by protolytic transamination [Eq. (b)] have established η^2-bound pyrazolato ligands in d-block transition metal complexes as a general feature. Moreover, their presence in compounds such as **1** and **2** cannot be related to the need for coordinative saturation, since these complexes are 16-electron systems. In addition, the formation of **2** indicates that **1** is not sterically saturated (eight-coordinate Ti^{4+} and Ta^{5+} have similar ionic radii[16]). The formation of homoleptic, coordinative, and sterically unsaturated tetrakis(η^2-pyrazolato)titanium(IV) complexes **1** (R = Me or Ph) can be attributed to the use of a noncoordinating solvent with an elevated boiling point (toluene). This discourages coordination of an additional ligand, for example the low-boiling dimethylamine product [Eq. (b)]. There is the possibility of coordination of R_2pzH (R = Me, Ph) to give $[Ti(R_2pz)_4(R_2pzH)]$, as in the synthesis of $[La(tBu_2pz)_3(tBu_2pzH)_2]$ (Ln = La, R = tBu, R′ = Ph) in Equation (a) in low-boiling petroleum ether.[17] The higher boiling point of toluene obviates this in Equation (b).

$$[M(NMe_2)_n] + n\,R_2pzH \longrightarrow [M(R_2pz)_n] + n\,HNMe_2 \qquad \text{(b)}$$

Winter et al. provided a bonding model based on ab initio calculations[1] for the $[Ti(\eta^2\text{-}R_2pz)_4]$ complexes in which electron density from the nitrogen lone pairs is placed in molecular orbitals which interact with appropriate empty d orbitals on Ti. In the calculations η^1-coordination did not constitute a minimum, and it was proposed that the presence of empty d orbitals favors η^2-bonding over η^1-bonding.[1] On this basis, the formation of $[Ta(\eta^2\text{-}Me_2pz)_3(\eta^1\text{-}Me_2pz)_2]$ is surprising. The alternative formation of $[Ta(\eta^2\text{-}Me_2pz)_5]$ is unlikely, since it is a formal 20-electron system, but $[Ta(\eta^2\text{-}Me_2pz)_4(\eta^1\text{-}Me_2pz)]$ is plausible. The steric coordination number[18] of η^2-Me$_2$pz is 1.54,[14] whereas that of η^1-Me$_2$pz should be comparable with that of one end of a bridging Me$_2$pz group (1.37). Therefore, the sum of the steric coordination numbers of the ligands in $[Ta(\eta^2\text{-}Me_2pz)_5]$ (7.7) is high for an ion of the size[16] of Ta^{5+}, and it reduces to 7.4 in $[Ta(\eta^2\text{-}Me_2pz)_3(\eta^1\text{-}Me_2pz)_2]$, which evidently provides the most stable steric/electronic balance (formally 16 electrons). Based on the calculations it was predicted that η^2-binding will be observed in early to middle transition metal complexes.[1] For ions of the same charge, steric factors also favor a change from η^2 to η^1 over the series. It is of interest both to test this prediction and to establish whether steric or electronic factors are dominant in determining the bonding mode.

The biggest challenge now is to achieve η^5-pyrazolate coordination (type **II**). Azacyclopentadienes can form π bonds, since η^5-bonding of the 2,5-di-*tert*-butylpyrrolyl ligand is known for main group, d-block, and f-block metals,[19] but in this case binding of nitrogen to metals is substantially blocked. It will take more ingenuity to achieve this outcome for pyrazolate ligands.

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