Ta(CNXYl)$_6$: An Isocyanide Analogue of Hexacarboxyltantalum(0)**

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In memory of Alan Davison (1936–2015)

Abstract: Hexakis(2,6-dimisopropylphenylisocyanide)tantalum is the first isocyanide analogue of the highly unstable Ta(CO)$_6$ and represents the only well-defined zerovalent tantalum complex to be prepared by conventional laboratory methods. Two prior examples of homoleptic Ta$i$ complexes are known, Ta(benzene)$_6$ and Ta(dmpe)$_6$, dmpe = 1,2-bis(dimethylphosphino)ethane, but these have only been accessed via ligand co-condensation with tantalum vapor in a sophisticated metal-atom reactor. Consistent with its 17-electron nature, Ta(CNXYl)$_6$ undergoes facile one-electron oxidation, reduction, or disproportionation reactions. In this sense, it qualitatively resembles V(CO)$_6$, the only paramagnetic homoleptic metal carbonyl isolable under ambient conditions.

In contrast to vanadium and niobium,$\textsuperscript{[1]}$ isolable homoleptic complexes of zerovalent tantalum are quite rare, with only two examples presently known: Ta(benzene)$_6$,$\textsuperscript{[2]}$ and Ta(dmpe)$_6$,$\textsuperscript{[3]}$ dmpe = 1,2-bis(dimethylphosphino)ethane. Also, these species are very poorly accessible because they are only available via tantalum vapor synthesis methods, which require specialized metal-atom reactors.$\textsuperscript{[4]}$ Although Ta(bipy)$_6$, bipy = $\alpha,\alpha'$-bipyridine,$\textsuperscript{[5]}$ and Ta(ip$_2$Pr$_2$-dad)$_6$, ip$_2$Pr$_2$-dad = 1,4-diisopropyl-1,4-diazabuta-1,3-diene,$\textsuperscript{[6]}$ were originally suggested to be zerovalent tantalum complexes, later experimental and computational studies indicate that both compounds contain high-valent Ta$^{VII}$.$\textsuperscript{[7]}$

Perhaps the most interesting comparisons of homoleptic zerovalent complexes of Group 5 metals are for the 17-electron hexacarbonyls of these species: V(CO)$_6$ is well-known as the only paramagnetic unsubstituted metal carbonyl isolable under ambient conditions,$\textsuperscript{[8]}$ while Ta(CO)$_6$,$\textsuperscript{[9]}$ and Nb(CO)$_6$,$\textsuperscript{[10]}$ have only been obtained at low temperatures as matrix isolated species and may be unstable above 50 K. Barybin’s synthesis of the 17-electron complex V(CNXYl)$_6$, Xyl = 2,6-dimethylphenyl, which was far more thermally stable (m.p. 159–160°C decom.)$\textsuperscript{[11]}$ than V(CO)$_6$ (decomp. 60–70°C),$\textsuperscript{[8]}$ suggested that Ta(CNXYl)$_6$, and the niobium analog might be isolable. However, despite success in the synthesis and isolation of [Ta(CNXYl)$_6$]$^-$, [Ta(CNXYl)$_6$]$^{1-}$, and related complexes,$\textsuperscript{[11,12]}$ attempts to isolate the corresponding elusive neutral homoleptic tantalum and niobium complexes uniformly failed.$\textsuperscript{[13]}$ Many years ago Mann, Gray, and Hammonds reported on the zerovalent complex W(CNXYl)$_6$, Dipp = 2,6-diisopropylphenyl,$\textsuperscript{[14]}$ and it was of interest to determine whether this more sterically encumbered isocyanide could stabilize the corresponding neutral tantalum complex. Initial results were promising and provided a structural characterization of the unique ditantalum salt [Ta(Ta(CNXYl)$_6$)],$\textsuperscript{[15]}$ a type of compound previously unknown for homoleptic metal carbonyls and isocyanides,$\textsuperscript{[16]}$ and of significance as a formal disproportionation product of the desired Ta(CNXYl)$_6$ complex. Unfortunately, this salt could not be obtained as a pure bulk solid and the neutral species was not isolated, so this project was temporarily abandoned. Now more than a decade later, independent syntheses of both the cation and anion in the ditantalum salt, [Ta(CNXYl)$_6$][BF$_4$]$_2$, $\textsuperscript{(1)}$,$\textsuperscript{[17]}$ and K[Ta(CNXYl)$_6$]$_2$, $\textsuperscript{(3)}$, respectively, were developed, as well as the synthesis and isolation of neutral Ta(CNXYl)$_6$, Ta(CNXYl)$_6$ is the first fully substituted derivative of Ta(CO)$_6$, containing monodentate ligands,$\textsuperscript{[18a]}$ and is the only one to be obtained by a conventional synthesis.$\textsuperscript{[18b]}$ The niobium analogue has also been isolated and structurally characterized.$\textsuperscript{[19]}$

The deep red-brown and very air sensitive precursor complex Ta(CNXYl)$_6$, $\textsuperscript{(2)}$, was obtained in 90% yield by the reaction of I$_2$ with [E$_2$N][Ta(CO)$_6$]$^{2a}$ in the presence of six equivalents of CNDDimp in tetrahydrofuran, THF. A similar procedure was previously used for the synthesis of Ta(CNXYl)$_6$.$\textsuperscript{[11]}$ However, the reaction mixture leading to $\textsuperscript{2}$ also had to be heated at reflux for 20 h to avoid contamination by mixed carbonyl-isocyanides.$\textsuperscript{[20]}$ IR and NMR spectra, as well as the molecular structure of $\textsuperscript{2}_{\text{cis}}$,$\textsuperscript{[21]}$ are very similar to those previously reported for the CNXYl analogue.$\textsuperscript{[11]}$ Reduction of $\textsuperscript{2}$ by a minimum of 3 equivalents of KC$_8$ in toluene over a period of 5 days at 20°C was necessary for high conversion to satisfactorily pure dark violet microcrystalline K[Ta(CNXYl)$_6$]$_2$, $\textsuperscript{3}$, isolated in 70–80% yields.$\textsuperscript{[22]}$

Treatment of cold, −65°C, deep red solutions of $\textsuperscript{3}$ in toluene with one equivalent of solid Ph$_2$PdAuCl afforded within 2 h a bright green solution of Ph$_2$PdAuTa(CNXYl)$_6$, $\textsuperscript{(4)}$ which was isolated in 79% yield as violet-brown microcrystals. Although gold derivatives of metal carbonyls have
The synthesis of \(\text{Ph}_3\text{Me} = \text{R}\) has been achieved thereby forming, and \(\text{MoO}_3\) attempts to oxidize 3 are nearly superimposable in this regard, and we believe the formal disproportionation product of 5 is stable only in the solid state. Figueroa’s group reported very similar comproportionation reactions of [Co(CNAr)_3](THF), \(n = 0, 1, 2\); with [Co(CNAr)_3] to quantitatively produce the second known 17-electron homoleptic isocyanide metal(0) complex, Co(CNAr)_6, where Ar is an extremely bulky m-terphenyl group, 2,6-bis(2,4,6-trimethyl-phenyl)phenyl. The second reaction with [Et,NH][BPh_4] was an attempt to protonate 3 to give the unknown hydride, HTa(CNPh). But unlike HTa(PF_6), which is fairly robust, no evidence for the isocyanide hydride was obtained. Isocyanide metal hydrides are rare species and Figueroa and co-workers recently reported [HFe(CNAr)_3] and [HCo(CNAr)_3].

Solution IR spectra of 5 are nearly superimposable in unreactive solvents, including alkanes, arenes, and THF. In THF, one intense broad \(\nu(CN)\) peak is present at 1934 cm\(^{-1}\), similar to that of \(\nu(CN)(\text{Xyl})_2\), 1939 cm\(^{-1}\), and those reported for tungsten analogs, W(CNAr)_6, Ar = Xyl, 1934 cm\(^{-1}\); Dipp, 1944 cm\(^{-1}\) (KBr disk); \(1944\) cm\(^{-1}\) \((\text{H})\) and \(13\)C NMR spectra of 5 in [D_8]THF show paramagnetically shifted resonances in positions similar to those reported for V(CNPh)_6. Attempts to obtain reliable solution magnetic data for 5 by the Evans NMR method were unsuccessful due to its poor solubility in hydrocarbons, ethers and other unreactive solvents. However, as measured by SQUID magnetometry, the effective magnetic moment of solid 5 at 300 K is 2.03 \(\mu_B\), and decreases with decreasing temperature to 1.76 \(\mu_B\) at 2 K, consistent with an \(S = \frac{1}{2}\) spin centered on the Ta atom. The cyclic voltammogram of 5 in 1,2-difluorobenzene displays a reversible [Ta(CNPh)]\(_{10}^\text{+}^-\) redox couple centered at \(E_0 = -2.03\) V versus \(\text{Fc}^\text{0/1}^\text{+}\). Interestingly, this value is close to the reversible couple observed for \(\nu(CN)(\text{Xyl})_2\) \(1944\) V, but is about 1.5 V more negative than that of \(\nu(CO)(\text{Xyl})_2\) \(1944\) V, both measured under the same conditions in this study. Also, it should be noted that crystalline 5 exhibits remarkable thermal stability and decomposes without melting at 236–240°C, more than 70°C higher than the decomposition point previously reported for V(CNPh)_6.

Single crystals of 5 were grown from THF/pentane and consisted of dichroic golden-red brown plates of composition Ta(CNPh)_6 · 2THF and space group \(R3\). In the crystal

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**Figure 1.** Molecular structure of 4. Thermal ellipsoids are set at 50% probability, with hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles °: Ta–Au1 2.7207(2), Au1–P1 2.2737(8), Ta–C1 2.148(3), Ta–C14 2.150(3); average Ta–C–N 174(2), average C–N–C 165(8), Ta–Au–P 176.20(3).

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**Scheme 1.** Synthesis of Ph_3PAuTaL_6 and TaL_6, L = CNDipp, solvent = toluene.
structure, the metal atoms lie on inversion centers within the 3 axis, resulting in one independent isocyanide per unit cell. The two THF molecules are equivalent and located on a threefold axis. The molecular structure of 5 is shown in Figure 2.

Figure 2. Molecular structure of 5. Thermal ellipsoids are set at the 50% level with tetrahydrofuran of solvation and hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Ta1–C5 2.135(1), C1–N1 1.179(2), N1–C2 1.385(2); Ta1–C1-N1 176.9(1), C1–N1–C2 164.4(1), C1-Ta1-C1A 180.0, C1-Ta1-C1B 86.07(5), C1-Ta1-C1C 93.93(5).

with selected distances and angles. Six discrete isocyanide ligands are present in which the isocyanide terminal carbons form a slightly distorted octahedron about the tantalum. However, unlike V(CO)$_4$ and V(CN$_2$)$_2$, which show small degrees of tetragonal distortion in the M–C distances owing to a possible Jahn–Teller effect, as anticipated for low spin d$^3$ octahedral complexes, all M–C distances of 5 are identical by symmetry in the crystalline lattice.

The interatomic parameters of 5 appear to be normal compared to those of W(CN$_2$)$_2$. Thus, the Ta–C distance of 2.135(1) Å is approximately 0.07 Å longer than the average W–C distance, 2.062(2) Å, consistent with the larger atomic radius of Ta, 1.43 Å, relative to W, 1.37 Å.[27] However, the average WC–N distance, 1.176(4) Å, is essentially identical to the value observed for 5, 1.179(2) Å, which is in agreement with the nearly identical values observed for the most intense infrared CN stretching frequencies for both species. Also of interest is that the C-N-C bend angles of 5, 164.4(1)$^\circ$, and of W(CN$_2$)$_2$, 164.2(1)$^\circ$, are statistically identical, indicative of similar degrees of metal(d$^3$) to π*(CN$_2$) back-bonding in these otherwise analogous 17- and 18-electron formally zerovalent metal complexes, respectively.

Comparisons of the reactivity patterns of 5 and V(CO)$_4$ provided some surprises. The V(CO)$_4$ complex undergoes facile nucleophilic substitution[30] and Lewis-base-induced disproportionation[34] reactions, consistent with its 17-electron metalloradical nature,[35] but in these reactions 5 often proved to be much less reactive. For example, whereas V(CO)$_4$ undergoes full disproportionation, rapidly in THF[36] and slowly in toluene at 20 °C,[37] 5 is stable for at least a week in these solvents and may even be briefly heated to 60 °C for about 5 min without change. This stability is likely due to both the crowded nature of the CNDipp ligand, which protects 5 from nucleophilic attack, and its stronger donor/weaker acceptor character compared to CO.[38] Also, for example, trimethylphosphate reacts with V(CO)$_4$ in hexane at 20 °C to afford the salt [V(CO)$_4$(PMe$_3$)$_2$][V(CO)$_2$],[39] whereas no reaction with 5 occurs under the same conditions. More basic pyridine also causes full and irreversible disproportionation of V(CO)$_4$,[34,38] but addition of 5 to neat pyridine at 20 °C affords only a reversible disproportionation process, from which pure 5 is isolated on removal of solvent.[40] In contrast, the more basic triphenylstannyln anion, [Ph$_3$Sn]$^-$, reacts with 5 quantitatively within minutes to give high isolated yields of the disproportionation products Ph$_3$SnTa(CNDipp)$_4$ (6) and [K(18-crown-6)][Ta(CDipp)$_2$] (7) according to Eq. (1), L = CNDipp.

$$2\text{TaL}_4 + [\text{K(18-crown-6)}][\text{Ph}_3\text{Sn}] \rightarrow \text{Ph}_3\text{SnTaL}_4 + [\text{K(18-crown-6)}][\text{TaL}_4]$$

Product 6 has also been isolated in about 80% yield via the more conventional reaction of K[Ta(CNDipp)$_2$] with Ph$_3$SnCl, analogous to the same route used by Davison 45 years ago for the synthesis of Ph$_3$SnTa(CO)$_4$ from [Ta(CO)$_4$]$_2$.[41] Interestingly, 6 represents the first isolable tin adduct of a homoleptic isocyanide of a Group V metal, M(CN$_2$)$_2$. M = V, Nb, Ta. Warnock and Cooper prepared Ph$_3$SnCo(CN$_2$)$_2$ in 1989 as a key derivative in their characterization of the first homoleptic isocyanidemetalate, [Co(CN$_2$)$_2$].[42]

Because the homoleptic cobalt isocyanides, Co$_2$(CN$_2$)$_2$, R = iBu[43] and Xyl[44] were reported to react with carbon monoxide (R = iBu, rapidly at 20°C under 1 atm; R = Xyl, slowly at 40°C under 30 atm) to afford the respective salts [Co(CN)$_2$][Co(CO)$_4$], the reaction of 5 with CO was examined. Treatment of deep red-violet solutions of 5 with CO (1 atm) at −65°C within seconds gave a dark green solution (of unknown nature). On warming to 20°C, the solution had changed to a transparent deep red color. The reaction was monitored by IR spectroscopy and had to be heated to 60°C under CO for 4 days to afford the final product, [Ta(CDipp)$_2$][Ta(CO)$_4$(CNDipp)$_2$] (8) isolated as satisfactorily pure dark red-brown microcrystals in 67% yield, Eq. (2), L = CNDipp.

$$2\text{TaL}_4 + 5\text{CO} \rightarrow \text{TaL}_4[\text{Ta(CO)}_4]\text{L} + 4\text{L}$$

Single crystal X-ray structural characterization of 8 shows well defined and discrete [Ta(CN$_2$)$_2$]$^-$ and [Ta(CO)$_4$]$_i$ ions in the crystalline lattice.[24] The production of salt 8 is very reminiscent to Sattelberger’s synthesis of [Ta(CO)$_4$(PMe$_3$)$_2$][Ta(CO)$_2$(PMe$_3$)$_2$] in 83% yield via the carbonylation of Ta(BH$_4$)$_3$(CO)$_2$(PMe$_3$)$_2$ in the presence of PMe$_3$.[45] It is tempting to suggest that his ditantalum salt
arose via the CO promoted disproportionation of an unobserved 17-electron Ta-storage complex, Ta(CO)$_6$[PF$_6$], and only one rather thermally unstable species of this type has been claimed, Ta(CO)$_5$(dppe), dppe = 1,2-bis(diphenylphosphino)ethane, but unfortunately this potentially significant material has not been obtained in pure form or structurally authenticated, nor has it its reaction with CO or other donor ligands been reported. For example, the well-characterized and presumably less reactive 17-electron complex V(CO)$_5$(dppe)$_2$, whereas it reacts further with dppe to provide the robust 17-electron species trans-V(CO)$_5$(dppe)$_2$. It has long been known to undergo disproportionation with bipy to afford the salt [V(bipy)$_2$][V(CO)$_5$(dppe)], whereas it reacts further with dppe to provide the robust 17-electron species trans-V(CO)$_5$(dppe)$_2$. In contrast to S, V(CNXyl)$_6$ reacts slowly with ambient pressures of CO at 60°C in THF over a 24-h period to afford quantitative yields of the previously reported trans-V(CO)$_5$(CNXyl)$_2$. No evidence for disproportionation was noted in this reaction, similar to the reaction of V(CO)$_5$ with CO. The latter is known to slowly exchange with CO at 20°C, but does not undergo disproportionation in the solid state or in unreactive solvents in the presence or absence of CO.

In summary, access of Ta(CN)(dppe)$_2$ affords the first example of an isolable 17-electron and formally zerovalent Ta$_4$ species. Its facile synthesis promises to open up a distinctly new area of 5d-block isocyanide chemistry, because no prior example of a paramagnetic complex of this type is known. EPR spectral properties of 5 are under examination and will be presented elsewhere.

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Conflict of interest

The authors declare no conflict of interest.

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[13] Infrared evidence for the production of Ta(CN)Xyl in solution was obtained on several occasions (with a v(CN) value very similar to that of 5 herein), but the species invariably decomposed on attempted isolation. M. V. Barybin, A. Romanenkov, J. E. Ellis, unpublished research, 1998 – 2002.


[15] W. W. Brennessel, A. Romanenkov, J. E. Ellis, unpublished research, 2002. The single-crystal X-ray study shows separate [Ta(CN)(dppe)$_2$]$_2$ and [Ta(CN)(dppe)$_2$]$_2$ units, which have nearly identical structures to those previously reported for [Ta(CN)Xyl]$_2$[BF$_4$] and [Ca(Ta(CN)Xyl)$_2$], respectively[11] Details of this structure will be reported separately. Crystal data: C$_7$H$_{18}$N$_2$Ta$_2$, triclinic, P1; cell constants a = 14.1843(8), b = 23.048(1), c = 25.273(1) Å, α = 82.674(1), β = 75.610(1), γ = 89.419(1)°, V = 7935.8(8) Å$^3$, Z = 2, T = 173(2) K, 74364 reflections (26336 for [I > 2σ(I)]; R = 0.0553; wR = 0.0815 (all data).

[16] Mixed carbonyl-isocyanide salts, such as [Co(CN)(CO)$_3$], are well known, e.g., Y. Yamamoto, H. Yamanaka, Inorg. Chem. 1978, 17, 3111, but to our knowledge salts containing homoleptic [ML$_n$]$_2$[ML]$_n$ units for the identical metal and ligand, L = CO,CNR, or other acceptor groups, have not been previously reported.

[17] Compound 1 was obtained by the analogous procedure used in the synthesis of [Ta(CNXY)4][BF4]. See Supporting Information.


[19] Satisfactorily pure Nb(CNXY)5 has been isolated in 84% yield from the reaction of bis(mesitylene)niobiurn(0) with 6 equivalents of CNBDipp in THF. Details of this study will be presented elsewhere. C. J. Roberts, V. G. Young, J. E. Ellis, unpublished research (2013 – 2015). Crystal data: C6H9N2Ta, monoclinic, P21/n; cell constants a = 12.192(3), b = 43.57(1), c = 13.981(4) Å, α = 90, β = 100.592(6), γ = 90°; V = 7300(3) Å3, Z = 4, T = 173(2) K; 21,272 reflections (2606 for I > 2σ(I)); R1 = 0.0393; wR2 = 0.0986 (all data).


[21] Details of the structure of 2 will be reported separately. Crystal data: C8H12TaN4, monoclinic, P21/n; cell constants a = 12.192(3), b = 43.57(1), c = 13.981(4) Å, α = 90, β = 100.592(6), γ = 90°; V = 7300(3) Å3, Z = 4, T = 173(2) K; 54,060 reflections (10,006 for I > 2σ(I)); R1 = 0.0403; wR2 = 0.0825 (all data).

[22] Stoichiometric amounts of KC8 are often employed in reductions, but as the potassium reacts the “Stage 1,” KC8 changes to “Stage 2,” KC8+, which is undoubtedly a weaker reducing agent (i.e. lower K-C ratio) and may be kinetically more inert towards release of additional potassium. See: N. N. Greenwood; A. Ear shaw, Chemistry of the Elements, 2nd ed., Butterworth-Heinemann, Oxford, 1997, pp. 293 – 295.

[23] Interestingly, [K2Ta(CNXY)3] could only be isolated as the [K4(cryptand 2.2.2)] salt. The unsolvated potassium salt, unlike Cs2[Ta(CNXY)4], was exceedingly unstable above 0°C, rapidly decomposing to uncharacterized oligomeric CNXY species. Also, solutions of Na2[Ta(CNBDipp)2] are quite stable in THF at 20°C under anaerobic conditions, unlike “Na2[Ta(CNXY)2]” which rapidly decomposes in solution above –40°C, in the absence of crown ethers or cryptands.


[29] We are unaware of the prior use of MoO3 as a selective oxidant in inorganic/organometallic synthesis, other than in the prepa ration of “molybdenum blues.” It can be anticipated that MoO3 will also be useful in the removal of alkali metals from other strongly reducing metalloids. Note also if the reaction of MoO3 with 3 is continued for ≥12 h at 20°C, significant oxidation of 5 is observed.


[38] An especially cogent comparison of the donor/acceptor character of the closely related CNXyl ligand versus CO has been described for trans-V(CO)2(CNXY)L14.


[40] See Supporting Information for discussion of the interaction of 5 with pyridine. Reactions of 5 with other solvents and neutral donors will be reported elsewhere.


[44] See Supporting Information for more details. CCDC 1551212(4), 1551214 (5), and 1551213 (8) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.


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