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Tris(1-4-η^4-anthracene)niobate(1-), the first polyaromatic hydrocarbon complex of niobium†

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The first tris(arene)niobium complex, [Nb(1-4-η^4-anthracene)$_3$]$^-$, has been obtained by the sodium or potassium anthracene reduction of NbCl$_4$(THF)$_2$, structurally characterized by X-ray analysis and shown to undergo facile anthracene displacement reactions in the presence of excess CO, PF$_3$, 1,3,5,7-cyclooctatetraene and P(OMe)$_3$.

Polyarene transition metal complexes often undergo facile ligand substitution reactions resulting in the displacement of bound polyarenes.[1] In this sense, they may function as storable sources of highly unsaturated metal fragments.[1,2] Homoleptic complexes of this type are of particular significance since they may shed all coordinated polyarenes in reactions and thereby behave as 'naked' metal atom reagents.[3] Consequently, these species hold considerable promise as precursors for the general exploration of transition metal chemistry. In 1998 homoleptic polyareneniobates(1-) were proposed to be intermediates in the alkali metal naphthalene and anthracene mediated reductive carbonylations of NbCl$_4$(THF)$_2$, THF = tetrahydrofuran.[4] Determining the nature of these species has been of interest since no polyarene complexes of niobium have been characterized. In contrast, several examples of polyarene complexes of vanadium and tantalum are known.[5] Attempts to identify the niobium–naphthalene intermediate(s) have been unsuccessful to date; however, the corresponding anthracene complex has been isolated and characterized as tris(1-4-η^4-anthracene)niobate(1-), **1**.

Reduction of NbCl$_4$(THF)$_2$ (1.94 g, 5.12 mmol) with five equiv. of potassium anthracene in 300 mL of THF at −60 °C, as previously described in detail,[4] gave a red–violet solution after slowly warming to 20 °C over a period of 12 h. From this reaction mixture [K(THF)$_x$][**1**] was isolated as a free flowing homogeneous and very air sensitive bright red powder. Treatment of the latter with 18-crown-6 in THF gave sparingly soluble and satisfactorily pure orange–red microcrystals of [K(18-crown-6)(THF)[**1**] (4.24 g, 83% based on NbCl$_4$(THF)$_2$). By the same procedure, red microcrystalline [Na(triglyme)$_2$][**1**], triglyme = 1,2-bis(2-methoxyethoxy)ethane, was isolated in 76% yield. Salts of **1** were stable for days or months at 20 °C in solution (THF) or in the solid state, respectively, under an argon atmosphere. NMR properties of **1** were independent of cation and consistent with the proposed structure.‡ Single crystal X-ray analysis of [K(18-crown-6)(THF)][**1**] confirmed the formulation of **1** based on NMR data and elemental analyses.§ Overall, the structure of **1** (Fig. 1) is closely related to that of tris(η^4-naphthalene)zirconate(2-).[6] For example, the average dihedral angles of the bound rings and C–C distances of the η^4-diene units are statistically identical and indicate that the degree of metal π donation or backbonding to the respective polyarenes is very similar.[7]

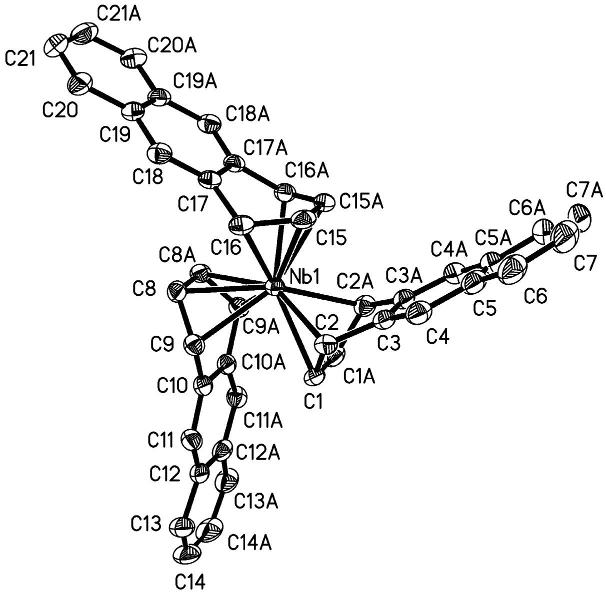

Fig. 1 Molecular structure of **1**; 50% probability thermal ellipsoids; hydrogens omitted for clarity. Selected bond lengths (Å): Nb–C(1), 2.387(2); Nb–C(2), 2.385(2); Nb–C(8), 2.395(2); Nb–C(9), 2.395(2); Nb–C(15), 2.381(2); Nb–C(16), 2.383(2); C(1)–C(1A), 1.371(4); C(1)–C(2), 1.442(3); C(8)–C(8A), 1.380(4); C(8)–C(9), 1.435(3); C(15)–C(15A), 1.372(4); C(15)–C(16), 1.441(3).

Excess CO readily reacts with **1** to provide an 82% isolated yield of [K(18-crown-6)(THF)$_2$][Nb(CO)$_6$], under the same conditions reported previously for the anthracene mediated synthesis of this carbonyl.[4] A variety of acceptor ligands, including organophosphanes, phosphites, polyenes and others also combine with **1** to displace one or more anthracene groups.[8] For example, excess (7 equiv.) 1,3,5,7-cyclooctatetraene, COT, and trimethylphosphite react within seconds at 0 °C in THF with **1** to provide the previously known [Nb(COT)$_3$]$^-$,[9] and the unprecedented [Nb(η^4-C$_{14}$H$_{10}$)$_2$(P(OMe)$_3$)$_2$]$^-$, **2**, in 86% and 67% isolated yields as [K(18-crown-6)(THF)]$^+$ salts, respectively. Interestingly, the reaction of **1** with excess trimethylphosphite in refluxing THF for 15 h also only generated **2** in 59% isolated yield. No evidence for the formation of more highly substituted species, such as the unknown [Nb(P(OMe)$_3$)$_6$]$^-$, were obtained in any of these reactions. In contrast, the reaction of **1** with excess PF$_3$ (1 atm, −60 to +20 °C), gave a 50% isolated yield of the previously described [Nb(PF$_3$)$_6$]$^-$.[4]

NMR spectra of **2** are consistent with the presence of two identical η^4-anthracenes bound *via* peripheral rings to niobium and two equivalent trimethylphosphite ligands.‡ Single crystal X-ray analyses are in accord with the NMR data and establish that the coordination environment about niobium in **2** (Fig. 2) is approximately octahedral with *cis*-trimethylphosphite groups.§

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† Dedicated to Professor Michael F. Lappert on the occasion of his 75th birthday.

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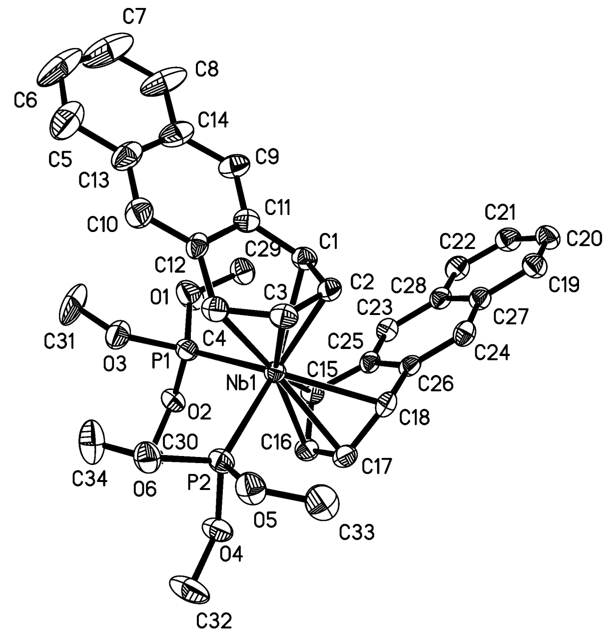

Fig. 2 Molecular structure of **2**; 50% probability thermal ellipsoids; hydrogens omitted for clarity. Selected bond lengths (Å) and angles (°): Nb–C(1), 2.460(3); Nb–C(2), 2.322(3); Nb–C(3), 2.309(3); Nb–C(4) 2.376(3); Nb–C(15), 2.418(3); Nb–C(16), 2.334(3); Nb–C(17), 2.334(3); Nb–C(18), 2.431(3); Nb–P(1), 2.507(1); Nb–P(2), 2.481(1); C(1)–C(2), 1.424(5); C(2)–C(3), 1.392(5); C(3)–C(4) 1.444(5); C(15)–C(16), 1.446(5); C(16)–C(17), 1.391(5); C(17)–C(18), 1.424(5); P(1)–Nb–P(2), 97.55°.

Interestingly, **1** and **2** have about the same average niobium–diene centroid distances (**1**, 2.037(7); **2**, 2.022(6) Å) suggesting that the replacement of one η^4-anthracene unit in **1** by the two $P(OMe)_3$ groups in **2** does *not* substantially change the niobium–anthracene bond strength. Also, the presence of nearly identical average C–C distances for the outer and inner carbons of the coordinated diene units of **1** and **2** indicate a similar degree of niobium to anthracene back bonding for both species.[7] Thus, the reluctance of **2** to react with additional trimethylphosphite appears to be mainly due to steric crowding about the niobium center, owing to the presence of the two coordinated phosphites. In contrast, **2** rapidly reacted with the smaller CO ligand (excess CO, 1 atm, 0 °C) to give a mixture of the previously known $[Nb(CO)_5(P(OMe)_3)]^-$ and *cis*-$[Nb(CO)_4(P(OMe)_3)_2]^-$.[10]

In conclusion, sodium or potassium anthracene reductions of $NbCl_4(THF)_2$ in THF provided 75–83% isolated yields of [Nb(1-4-η^4-anthracene)$_3$]$^-$, **1**, which was shown to be substitutionally labile in reactions with CO, PF_3, 1,3,5,7-cyclooctatetraene, and $P(OMe)_3$. Compound **1** is not only the first polyarene complex of niobium but also is the only known homoleptic anthracene complex of a second row (4d) metal. This study and prior ones[2,3] underscore the special utility of alkali metal anthracenes in accessing unprecedented bis- or tris(anthracene)metal complexes, which are convenient sources of highly unsaturated transition metal fragments in synthesis. Extension of these studies to other polyaromatic hydrocarbons and metals are currently in progress in this laboratory.

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Notes and references

‡ Satisfactory elemental analyses (C, H) were obtained for all new compounds. [K(18-crown-6)(THF)][**1**]; ^{1}H NMR (300 MHz, [$^2H_8$] THF, 20 °C, $SiMe_4$, resonances due to 18-crown-6, THF omitted, labeling of C,H as per Fig. 1): δ 3.44 (m, 6H, H_2), 3.62 (m, 6H, H_1), 6.37 (s, 6H, H_4), 6.83 (m, 6H, $H_{6\text{ or }7}$), 7.17 (m, 6H, $H_{7\text{ or }6}$). $^{13}C\{^1H\}$ (75 MHz): δ 66.0 (s, C_2), 111.0 (s, C_1), 113.0 (s, C_4), 122.7 (s, $C_{6\text{ or }7}$), 126.2 (s, $C_{7\text{ or }6}$), 135.0 (s, C_5), 149.5 (s, C_3) ppm. Assignments based on ^1H–^{13}C heteronuclear multiple quantum correlation (HMQC) and trends previously established for η^4-anthracene complexes,[2,3] but no unique assignment of C_6, C_7 or corresponding hydrogens was possible based on these data. [K(18-crown-6)(THF)][**2**]; ^{1}H NMR (300 MHz, [$^2H_8$] THF, 20 °C, $SiMe_4$, resonances due to 18-crown-6, THF omitted, labeling of C,H as per Fig. 2): δ 2.15 (br, 4H, $H_{1,4}$), 3.32 (d, 18H, $P(OMe)_3$), 4.80 (br, 4H, $H_{2,3}$), 5.70 (s, 4H, $H_{9,10}$), 6.50 (m, 4H, $H_{5,8\text{ or }6,7}$), 6.69 (m, 4H, $H_{6,7\text{ or }5,8}$). $^{13}C\{^1H\}$ (75 MHz): 50.8 ($P(OMe)_3$), 110.5 (s, $C_{9,10}$), 121.2 (s, $C_{5,8\text{ or }6,7}$), 124.4 (s, $C_{6,7\text{ or }5,8}$), 134.2 (s, $C_{13,14}$), 151.4 (s, $C_{11,12}$). Metal coordinated carbon atoms could not be resolved. Assignment of C, H resonances was established on the same basis as described above for **1**, $^{31}P\{^1H\}$ NMR (121 MHz, ref H_3PO_4) δ 204 (br, $P(OMe)_3$) ppm.

§ *Crystal data* for [K(18-crown-6)(THF)][**1**]: $C_{58}H_{62}KNbO_7$, M = 1003.09, orthorhombic, space group P_{nma}, a = 25.078(2), b = 11.7341(7), c = 16.4872(9) Å, V = 4851.6(5) Å^3, T = 173 K, Z = 4, μ(Mo–Kα) = 0.389 mm^{-1}, 29977 reflections collected, 5846 unique (R_{int} = 0.0531). Refinement on F^2, final $R1$ = 0.0342 (for 4199 reflections with $I > 2\sigma(I)$), $wR2$ = 0.0840 (for all data).

Crystal data for [K(18-crown-6)(THF)][**2**]: $C_{50}H_{70}KNbO_{13}P_2$, M = 1073.01, triclinic, space group P-1, a = 13.685(2), b = 13.686(2), c = 14.975(2) Å, α = 90.733(3), β = 100.912(2), γ = 113.307(2)°, V = 2517.2(6) Å^3, T = 173 K, Z = 2, μ(Mo–Kα) = 0.448 mm^{-1}, 14809 reflections collected, 8767 unique (R_{int} = 0.0331). Refinement on F^2, final $R1$ = 0.0448 (for 6418 reflections with $I > 2\sigma(I)$), $wR2$ = 0.1084 (for all data).

CCDC reference numbers 190190 and 190191. See http://www.rsc.org/suppdata/cc/b2/b207062f/ for crystallographic data in CIF or other electronic format.

1 E. P. Kündig and P. L. Timms, *J. Chem. Soc, Chem. Commun.*, 1977, 912; C. Elschenbroich and R. Möckel, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 870; J. A. S. Howell, N. F. Ashford, D. T. Nixon, K. C. Kola, T. A. Albright and S. K. Kang, *Organometallics*, 1991, **10**, 1852; S. Sun, L. K. Yeung, D. A. Sweigart, T.-Y. Lee, S. S. Lee, Y. K. Cheung, S. R. Switzer and R. D. Pike, *Organometallics*, 1995, **14**, 2613 and references therein.

2 J. K. Seaburg, P. J. Fischer, V. G. Young Jr. and J. E. Ellis, *Angew. Chem., Int. Ed. Engl.*, 1998, **37**, 155.

3 W. W. Brennessel, V. G. Young Jr. and J. E. Ellis, *Angew. Chem., Int. Ed.*, 2002, **41**, 1211.

4 M. V. Barybin, J. E. Ellis, M. K. Pomije, M. L. Tinkham and G. F. Warnock, *Inorg. Chem.*, 1998, **37**, 6518.

5 F. Calderazzo and G. Pampaloni, *J. Organometal. Chem.*, 1995, **500**, 47; K. Jonas and V. Wiskamp, *Z. Naturforsch.*, 1983, **38b**, 1113; M. K. Pomije, C. J. Kurth, J. E. Ellis and M. V. Barybin, *Organometallics*, 1997, **16**, 3582; J. D. Protasiewicz, P. A. Bianconi, I. D. Williams, S. Liu, C. P. Rao and S. J. Lippard, *Inorg. Chem.*, 1992, **31**, 4134; K. Mashima, Y. Nakayama, M. Kaidzu, N. Ikushima and A. Nakamura, *J. Organometal. Chem.*, 1998, **557**, 3.

6 M. Jang and J. E. Ellis, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1973.

7 C. Elschenbroich and A. Salzer, *Organometallics, A Concise Introduction*, 2nd edn., VCH, Weinheim, Germany, 1992, pp. 262–265.

8 W. W. Brennessel, O. E. Woisetschläger, S. N. Roush and J. E. Ellis, unpublished research.

9 L. J. Guggenberger and R. R. Schrock, *J. Am. Chem. Soc.*, 1975, **97**, 6693.

10 H.-C. Bechtold and D. Rehder, *J. Organomet. Chem.*, 1982, **233**, 215; G. F. Warnock, Ph. D. Thesis, University of Minnesota, 1985.