## THE METALLATION AND HYDROGENATION OF ARYL RINGS IN EARLY TRANSITION METAL ARYLOXIDE SYSTEMS

## **ROBERT W. CHESNUT, BRYAN D. STEFFEY and IAN P. ROTHWELL\***

Department of Chemistry, Purdue University, West Lafayette, IN 47907, U.S.A.

Abstract—The mixed chloro-aryloxide compounds of stoichiometry  $M(OAr-2,6Ph_2)_2Cl_3$ and  $[M(OAr-2,6Ph_2)_3Cl_2]$  (M = Nb, Ta; OAr-2,6Ph<sub>2</sub> = 2,6-diphenylphenoxide) serve as useful substrates for the synthesis of a series of corresponding tris- and bis-alkyl derivatives. Thermolysis of these alkyl compounds in hydrocarbon solvents leads to the formation of cyclometallated compounds of the type  $M(OC_6H_3Ph-C_6H_4)(OAr-2,6Ph_2)(R)_2$ and  $M(OC_6H_3Ph-C_6H_4)(OAr-2,6Ph_2)_2(R)$  (R = CH<sub>3</sub>, CH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-4Me). Reduction of the dichlorides  $M(OAr-2,6Ph_2)_3Cl_2$  with sodium amalgam in toluene solution does not yield the corresponding tris-aryloxides. Instead the bis-cyclometallated compounds  $M(OC_6H_3Ph-C_6H_4)_2(OAr-2,6Ph_2)$  (M = Nb, Ta) are produced in high yield along with H<sub>2</sub>. However, in the presence of one atmosphere of  $H_2$  the niobium compound undergoes reduction to produce Nb(OC<sub>6</sub>H<sub>3</sub>Ph- $\eta^4$ -C<sub>6</sub>H<sub>7</sub>)(OAr-2,6Ph<sub>2</sub>)<sub>2</sub>. Spectroscopic and structural studies of this latter compound show it to contain an  $\eta^4$ -bound cyclohexadiene ring formed by hydrogenation of an ortho-phenyl substituent of an aryloxide ligand. Treatment of the niobium cyclohexadiene complex with  $H_2$  (1000 psi, 25°C) leads to the hydrogenation of the original 2,6-diphenylphenoxide ligands to produce, after hydrolysis, high yields of 2,6dicyclohexylphenol. The selective side chain hydrogenation of 2,6-diphenylphoxide ligands can also be achieved by reacting alkyl compounds such as Nb(OAr-2,6Ph<sub>2</sub>)<sub>3</sub>Me<sub>2</sub> with H<sub>2</sub>. In this latter case a mono-hydride of stoichiometry  $Nb(H)(OAr-2,6cy_2)_4$  was isolated and structurally characterized.

The high valent early *d*-block, lanthanide and actinide metal-hydride and metal-alkyl bonds have been shown over the last few years to be extremely important functional groups, being implicated in a wide range of stoichiometric and catalytic reactivity.<sup>1-4</sup> Besides their ability to carry out the reduction of unsaturated small molecules and functionalities, a recently demonstrated reactivity of these metal hydrides and alkyls has been their propensity for activating a range of carbon-hydrocarbon bonds both intra- and intermolecularly.<sup>5-8</sup> An intriguing dual reactivity is demonstrated by their reactivity towards olefins.<sup>1,5-7</sup> By careful choice of the metal system and olefin substrate, both migratory insertion into metal-hydride or metal- alkyl bonds can be achieved: reactions of synthetic utility and relevance to catalytic processes. However, it is also possible to obtain metal  $\sigma$ -vinyl products resulting from activation of  $sp^2$ -CH bonds and elimination of either alkane or dihydrogen.<sup>5-7</sup> In the case of the related aromatic hydrocarbon substrates, either no reaction is observed or else ring metallation and formation of  $\sigma$ -aryl compounds is found to take place.<sup>5-8</sup> There is little evidence for arene hydrogenation occurring.9-12 During our studies of the early transition metal chemistry associated with sterically demanding aryloxide ligation<sup>8</sup> we have investigated the behaviour of 2,6diphenylphenoxide (OAr-2,6Ph<sub>2</sub>) as ancillary ligation for supporting organometallic chemistry.<sup>13,14</sup> This work, which is outlined here, has demonstrated that it is possible not only to induce intramolecular metallation of this ligand, <sup>13,14</sup> but that intramolecular hydrogenation of the side chain aryl groups by metal-hydride ligands can also be a directly competing reactivity.15

The chloride compounds  $M(OAr-2,6Ph_2)_2Cl_3$ and  $M(OAr-2,6Ph_2)_3Cl_2$  (M = Nb, Ta) prove to be useful substrates for the synthesis of simple alkyl derivatives containing 2,6-diphenylphenoxide ancillary ligation (Scheme 1).<sup>13,14</sup> However, the

<sup>\*</sup> Author to whom correspondence should be addressed.



(a)  $R=CH_3$ ; (b)  $R=CH_2C_8H_4(OAr)_2R$ OAr=2,6-diphenylphenoxide M=Nb, Ta

Scheme	1
Demonite	

simple methyl and 4-methylbenzyl derivatives are thermally unstable and undergo elimination of methane and *p*-xylene, respectively, to generate cyclometallated compounds. Structural studies<sup>14</sup> confirm the presence of six-membered metallacycle rings formed by the metallation of one of the side chain phenyl groups.<sup>8</sup> The use of labelled compounds such as Ta(OAr-2,6Ph<sub>2</sub>)<sub>3</sub>(CD<sub>3</sub>)<sub>2</sub> clearly shows that the reaction proceeds by loss of CD<sub>3</sub>H, indicating the absence of methylidene intermediates.<sup>8</sup> The use of 2,4,6-tri-aryl phenoxides that contain differing substituents attached to the 2- and 6-aryl ring shows that there is only a minor substituent effect on the rate of cyclometallation.<sup>16</sup>

Attempts to form low valent aryloxide compounds of niobium and tantalum by sodium amalgam reduction of  $M(OAr-2,6Ph_2)_3Cl_2$  (M = Nb, Ta) also leads to cyclometallated compounds. In this case, bis-cyclometallated compounds are obtained along with H<sub>2</sub> (Scheme 1).<sup>14,17</sup> A minor component was also observed in the reduction of the niobium compound. It is possible to generate this material in essentially quantitative yields by running the reduction under one atmosphere of H<sub>2</sub>. Spectroscopic and structural studies show this compound to be Nb(OC<sub>6</sub>H<sub>3</sub>Ph- $\eta^4$ -C<sub>6</sub>H<sub>7</sub>)(OAr-2,6Ph<sub>2</sub>)<sub>2</sub> in which one of the side chain aryloxide phenyl groups has undergone 1,2-hydrogenation (Scheme 2).<sup>15</sup> The resulting cyclohexadiene ring is then bound to the niobium in an  $\eta^4$ -fashion.<sup>18</sup> Hydrolysis of this material yields two equivalents of HOAr-2,6Ph<sub>2</sub>, along with one equivalent of 2-(cyclohex-2enyl)6-phenylphenol. A combination of 1D and 2D NMR experiments, as well as the use of deuterium labels, conclusively show that the two hydrogen atoms are added in a mutually cis-fashion. However, due to the unfavourable stereochemistry at the initial *ipso*-carbon the niobium metal centre has to bind to the opposite face of the cyclohexadiene unit to which the hydrogenation took place.18

Treatment of toluene solutions of the compound Nb(OC<sub>6</sub>H<sub>3</sub>Ph- $\eta^4$ -C<sub>6</sub>H<sub>7</sub>)(OAr-2,6Ph<sub>2</sub>)<sub>2</sub> with H<sub>2</sub> (1000 psi, 25°C, 6 days or 400 psi, 80°C, 6 h) results in the complete hydrogenation of all of the side chain phenyl rings. Hydrolysis allows the isolation of 2,6-dicyclohexylphenol in 85% isolated yield based on initial 2,6-diphenylphenoxide ligands. Partial hydrogenation followed by hydrolysis yields a mixture of 2,6-dicyclohexylphenol; 2-cyclohexyl-6-phenylphenol and 2,6-dicyclohexylphenol. Com-



Scheme 2.



Fig. 1. ORTEP view of Nb(H)(OAr-2,6cy<sub>2</sub>)<sub>4</sub> (molecule 2). Selected bond distances (Å) and angles (°) are

Nb(2)-O(210) 1.901(5)	1	Nb(2)—O(220) 1.901	(5)
Nb(2)-O(230) 1.863(5)	I.	Nb(2)O(240) 1.875	(5)
O(210)—Nb(2)—O(220)	176.2(2)	O(210)Nb(2)O(230	0) 89.8(2)
O(210)—Nb(2)—O(240)	89.8(2)	O(220)—Nb(2)—O(230	0) 89.9(2)
O(220)—Nb(2)—O(240)	90.3(2)	O(230)Nb(2)O(244	0) 177.5(2)

plete hydrogenation of the substituent phenyl rings can also be achieved by treating the dimethyl substrate, Nb(OAr-2,6Ph<sub>2</sub>)<sub>3</sub>Me<sub>2</sub>, or the bis-cyclometallated compound, Nb(OC<sub>6</sub>H<sub>3</sub>Ph-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>(OAr-2,6Ph<sub>2</sub>), with H<sub>2</sub>. Presumably initial formation of a dihydride intermediate (Scheme 2) takes place by hydrogenolysis of the Nb—C bonds. Analysis of the final reaction mixture by <sup>1</sup>H NMR spectroscopy indicates the presence of Nb—H functionalities as broad resonances in the  $\delta - 10-12$  region. In the case of the hydrogenation of Nb(OAr-2,6Ph<sub>2</sub>)<sub>3</sub> Me<sub>2</sub>, large orange blocks of stoichiometry Nb(H) (OAr-2,6cy<sub>2</sub>)<sub>4</sub> (OAr-2,6cy<sub>2</sub> = 2,6-dicyclohexylphenoxide) were obtained and structurally characterized (Fig. 1).\*

The use of 2,4,6-triphenylphenoxide ligation results in the formation of 2,6-dicyclohexyl-4-phenylphenol, with no evidence for hydrogenation of either the 4-phenyl substituent or the phenoxy ring. The use of deuterium as the reagent gas, as well as the use of asymmetric 2,6-di-arylphenoxide ligation, gives considerable mechanistic insight into these arene hydrogenation processes.

Acknowledgement—We thank the National Science Foundation (Grant CHE-8612063) for financial support of this research.

## REFERENCES

 (a) J. Schwartz and J. Labinger, Angew. Chem. Int. Ed. Engl. 1976, 15, 333; (b) E. I. Negishi, in Organometallics in Organic Synthesis. John Wiley, New York (1980); (c) N. M. Doherty and J. E. Bercaw, J. Am. Chem. Soc. 1985, 107, 2670.

<sup>\*</sup> Crystal data for Nb(H)(OAr-2,6cy<sub>2</sub>)<sub>4</sub> at 20°C: a =39.423(4), b = 22.577(6), c = 22.383(3) Å,  $\beta = 99.72(1)^{\circ}$ , Z = 12,  $d_{calc} = 1.165$  g cm<sup>-3</sup> in space group C2/c(No. 15). Of the 13,200 unique reflections collected,  $4 \leq 2\theta \leq 45^{\circ}$ , with Mo- $K_{\alpha}$  radiation, the 5771 with  $I > 3\sigma(I)$  were used in the final refinement to yield R = 0.057,  $R_w = 0.071$ . Hydrogen atoms were calculated assuming idealized geometry but were not refined. Two independent molecules were present in the unit cell, one (molecule 1) lying on a two-fold axis, while the other (molecule 2) occupies a general position. The niobiumhydride atom, which presumably lies above or below the square plane, could not be located. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

- 2. P. T. Wolczanski and J. E. Bercaw, Accts Chem. Res. 1980, 13, 121.
- (a) P. J. Fagan, E. A. Maata and T. J. Marks, in Catalytic Activation of Carbon Monoxide (Edited by P. C. Ford), ASC Symp. Series 152. American Chemical Society, Washington, D.C. (1981); (b) K. G. Moloy and T. J. Marks, J. Am. Chem. Soc. 1984, 106, 7051.
- 4. W. J. Evans, Adv. Organomet. Chem. 1985, 24, 131.
- 5. P. L. Watson and G. W. Parshall, Accts Chem. Res. 1985, 18, 51 and refs therein.
- (a) M. E. Thompson and J. E. Bercaw, Pure Appl. Chem. 1984, 56, 1; (b) M. E. Thompson, S. M. Baxter, A. R. Bulls, B. J. Burger, M. C. Nolan, B. D. Santarsiero, W. R. Schaefer and J. E. Bercaw, J. Am. Chem. Soc. 1987, 109, 203.
- J. W. Bruno, G. M. Smith, T. J. Marks, C. K. Fair, A. J. Schultz and J. M. Williams, J. Am. Chem. Soc. 1986, 108, 40 and refs therein.
- (a) I. P. Rothwell, *Polyhedron* 1985, 4, 177; (b) I. P. Rothwell, *Accts Chem. Res.* 1988, 21, 153; (c) L. D. Durfee and I. P. Rothwell, *Chem. Rev.* 1988, 88, 1059.
- (a) E. L. Muetterties and J. R. Bleecke, Accts Chem. Res. 1970, 12, 324; (b) J. W. Johnson and E. L. Muetterties, J. Am. Chem. Soc. 1977, 99, 7395; (c) L. S. Stuhl, M. Rakowski-DuBois, F. J. Kirsekorn, J. R. Bleecke, A. E. Stevens and E. L. Muetterties, J. Am. Chem. Soc. 1978, 100, 2405.

- (a) H. M. Feder and J. Halpern, J. Am. Chem. Soc. 1975, 97, 7186; (b) R. Wilczynski, W. A. Fordyce and J. Halpern, J. Am. Chem. Soc. 1983, 105, 2066.
- (a) M. J. Russell, C. White and P. M. Maitlis, J. Chem. Soc., Chem. Commun. 1977, 427; (b) M. A. Bennett, T.-N. Huang, A. K. Smith and T. W. Turney, J. Chem. Soc., Chem. Commun. 1978, 582; (c) M. A. Bennett, T.-N. Huang and T. W. Turney, J. Chem. Soc., Chem. Commun. 1979, 312.
- R. A. Grey, G. P. Pez and A. Wallo, J. Am. Chem. Soc. 1980, 102, 5948.
- R. W. Chesnut, L. D. Durfee, P. E. Fanwick, I. P. Rothwell, K. Folting and J. C. Huffman, *Polyhedron* 1987, 6, 2019.
- R. W. Chesnut, B. D. Steffey, I. P. Rothwell and J. C. Huffman, *Polyhedron* 1988, 7, 753.
- B. D. Steffey, R. W. Chesnut, J. L. Kerschner, P. J. Pellechia, P. E. Fanwick and I. P. Rothwell, J. Am. Chem. Soc. 1989, 111, 378.
- 16. R. W. Chesnut and I. P. Rothwell, results to be published.
- B. D. Steffey, L. R. Chamberlain, R. W. Chesnut, D. E. Chebi, P. E. Fanwick and I. P. Rothwell, Organometallics, in press.
- (a) G. Erker, C. Kruger and G. Muller, Adv. Organomet. Chem. 1985, 24, 1; (b) H. Yasuda, K. Tatsumi and A. Nakamura, Accts Chem. Res. 1985, 18, 120; (c) S. Datta, M. B. Fischer and S. C. Wreford, J. Organomet. Chem. 1980, 183, 353.