Inorg. Chem. **2003**, *42*, 7378–7380

Inorganic Chemistry
Communication

An Unprecedented Oxidative Migration of a Methyl Group from 2-(2′,6′-Dimethylphenylazo)-4-methylphenol Mediated by Ruthenium and Osmium

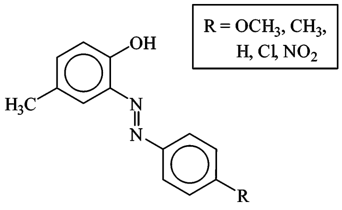
Rama Acharyya,[1a] Shie-Ming Peng,[1b] Gene-Hsiang Lee,[1b] and Samaresh Bhattacharya*,[1a]

Department of Chemistry, Inorganic Chemistry Section, Jadavpur University, Kolkata 700 032, India, and Department of Chemistry, National Taiwan University, Taipei, Taiwan, R.O.C.

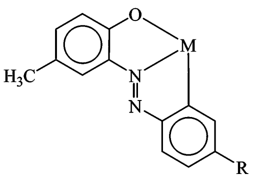
Received August 15, 2003

An unprecedented chemical transformation of 2-(2′,6′-dimethylphenylazo)-4-methylphenol has been observed upon its reaction with [$M(PPh_3)_3X_2$] (M = Ru, Os; X = Cl, Br) whereby one methyl group from the phenyl ring of the arylazo fragment migrates to the metal center via oxidation to CO.

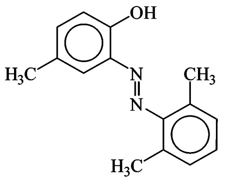
The present report has originated from our interest in the chemistry of platinum metal complexes of 2-(arylazo)-4-methylphenol (**1**).[2] It has been observed that upon reaction with different triphenylphosphine complexes of the platinum metals (e.g., [$Ru(PPh_3)_3Cl_2$], [$Os(PPh_3)_3Br_2$], [$Rh(PPh_3)_3Cl$], and [$Ir(PPh_3)_3Cl$]) ligand **1** always binds to the metal center as a tridentate C,N,O-donor (**2**) affording cyclometalated complexes.[2g−i,3] With the intention of inducing a different mode of coordination in such ligands, we selected 2-(2′,6′-dimethylphenylazo)-4-methylphenol (**3**), in which both the ortho positions of the phenyl ring in the arylazo fragment are blocked by methyl groups. In order to investigate the consequences of this ligand modification, reaction of **3** was carried out with the same triphenylphosphine complexes of the platinum metals listed above. In this Communication we disclose an interesting chemical transformation of **3** that took place during its reaction with the [$M(PPh_3)_3X_2$] (M = Ru, Os; X = Cl, Br) complexes.



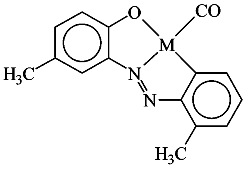
1



2



3



5

Reaction of **3** was first carried out with [$Ru(PPh_3)_3Cl_2$] in refluxing ethanol in the presence of triethylamine (containing 0.5% water), which afforded a deep green complex (**4**).[4] Though **3** contains three methyl groups, the ^1H NMR spectrum of **4** shows only two methyl signals at 1.82 and 2.31 ppm. The infrared spectrum of **4** shows a strong vibration at 1928 cm^{-1} indicating the possible presence of coordinated CO. The ^1H NMR and IR spectral data thus indicate that ligand **3** probably has undergone some unexpected chemical transformation during the course of the synthetic reaction. Identity of the green complex (**4**) has been revealed by its structure determination by X-ray crystal-

---

* Author to whom correspondence should be addressed. E-mail: samaresh_b@hotmail.com.

(1) (a) Jadavpur University. (b) National Taiwan University.

(2) (a) Chakravarty, J.; Bhattacharya, S. *Polyhedron* **1996**, *15*, 391. (b) Sinha, P. K.; Chakravarty, J.; Bhattacharya, S. *Polyhedron* **1996**, *15*, 2931. (c) Sinha, P. K.; Chakravarty, J.; Bhattacharya, S. *Polyhedron* **1997**, *16*, 81. (d) Pramanik, N. C.; Bhattacharya, S. *Polyhedron* **1997**, *16*, 3047. (e) Basuli, F.; Peng, S. M.; Bhattacharya, S. *Polyhedron* **1998**, *18*, 391. (f) Sui, K.; Peng, S. M.; Bhattacharya, S. *Polyhedron* **1999**, *19*, 631. (g) Dutta, S.; Peng, S. M.; Bhattacharya, S. *J. Chem. Soc., Dalton Trans.* **2000**, 4623. (h) Majumder, K.; Peng, S. M.; Bhattacharya, S. *J. Chem. Soc., Dalton Trans.* **2001**, 284. (i) Acharyya, R.; Basuli, F.; Wang, R. Z.; Mak, T. C. W.; Bhattacharya, S. Unpublished results.

(3) Lahiri, G, K.; Bhattacharya, S.; Mukherjee, M.; Mukherjee, A.; Chakravorty, A. *Inorg. Chem.* **1987**, *26*, 3359.

(4) Complex **4**: Ligand **3** (30 mg, 0.13 mmol) was dissolved in ethanol (40 mL), and to it were added triethylamine (containing 0.5% water) (22 mg, 0.22 mmol) and [$Ru(PPh_3)_3Cl_2$] (100 mg, 0.10 mmol). The mixture was then heated at reflux for 3 h to afford a deep brown solution. The solution was then evaporated to dryness to give a solid residue, which was subjected to purification by thin-layer chromatography on a silica plate. With benzene as eluant, a deep green band separated, which was extracted with acetonitrile. Upon evaporation of the acetonitrile extract complex **4** was obtained as a crystalline green solid. Yield: 40%. Calcd: C, 69.78%; H, 4.79%; N, 3.19%. Found: C, 69.37%; H, 4.82%; N, 3.14%. ^1H NMR: 1.82(CH_3); 2.31(CH_3); 5.91(d, 1H, $J = 8.6$); 6.05(s, 1H); 6.22(t, 1H, $J = 7.4$); 6.30(d, 1H, $J = 7.3$); 6.34(d, 1H, $J = 8.6$); 6.86(d, 1H, $J = 7.4$); 7.15−7.39(2PPh_3). ^{13}C NMR: 127.89, 129.84, 132.22 and 134.48 (2PPh_3); 19.59 (CH_3); 20.06 (CH_3); 116.53; 121.42; 121.51; 123.34; 128.19; 132.05; 132.40; 134.77; 135.99; 139.99; 141.96; 165.34 (Ru−C(Ar)); 173.67 (CO). ^{31}P NMR: 50.75 (s).

10.1021/ic034968i CCC: $25.00

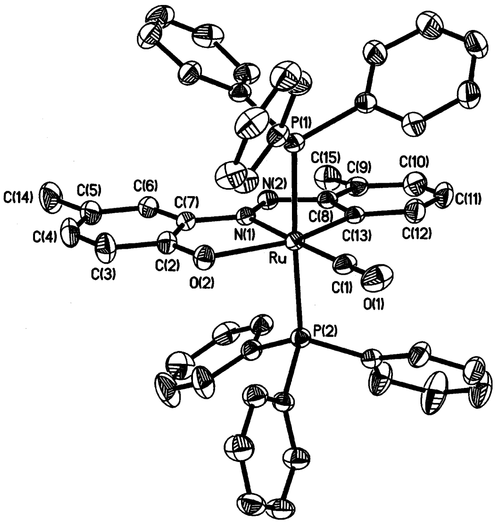


Figure 1. The molecular structure of **4**.

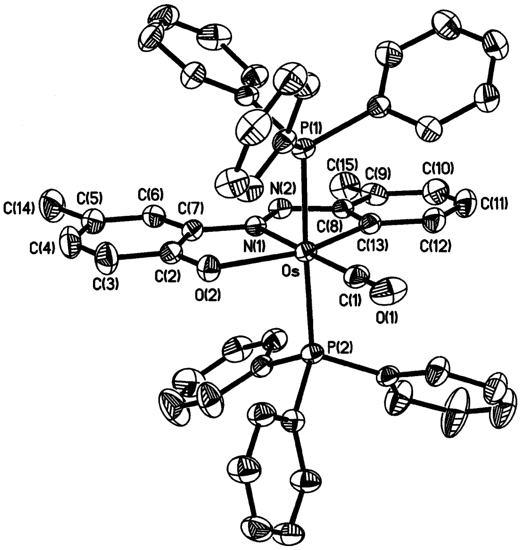
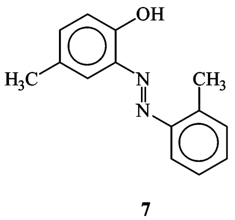


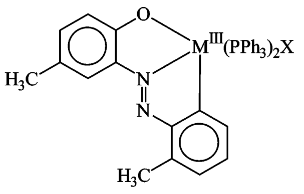
Figure 2. The molecular structure of **6**.

lography. The structure (Figure 1)[5] shows that upon reaction with [Ru$(PPh_3)_3Cl_2$] ligand **3** has indeed undergone an interesting chemical transformation, whereby one methyl group of **3** has migrated to the metal center via oxidation to CO and the modified ligand is coordinated to ruthenium as a dianionic C,N,O-donor ligand (**5**, M = Ru). Two PPh_3 ligands are also coordinated to ruthenium. The observed chemical transformation of **3** is not only unusual but also, to our knowledge, unprecedented.

To verify that the origin of the coordinated CO in complex **4** is the methyl group lost from ligand **3** and not the solvent (ethanol), reaction of ligand **3** with [Ru$(PPh_3)_3Cl_2$] has also been carried out in another alcoholic solvent that cannot undergo decarbonylation, viz., *tert*-butyl alcohol, as well as in a nonalcoholic solvent, viz., benzene, under refluxing conditions in the presence of triethylamine. The same green complex **4** has been obtained from these reactions,[6,7] which shows that the origin of CO is not the solvent. Furthermore, reaction of a similar ligand, viz., 2-(2′-methylphenylazo)-4-methylphenol (**7**), has been carried out with [Ru$(PPh_3)_3Cl_2$] in refluxing ethanol in the presence of triethylamine, which has afforded a cyclometalated complex of ruthenium(III) (**8**; M = Ru, X = Cl).[8] No loss of methyl group from this ligand **7** has taken place, and no carbonyl has been formed in this reaction. Results of the above experiments clearly show that the origin of the CO in complex **4** was not the alcoholic solvent but the displaced methyl group of ligand **3**.



7



8

Encouraged by the observed transformation of ligand **3** upon its reaction with [Ru$(PPh_3)_3Cl_2$], a similar reaction of it was also carried out with an analogous osmium complex, viz., [Os$(PPh_3)_3Br_2$], in order to check whether it again undergoes a similar transformation. The reaction afforded a light green complex (**6**),[9] which shows ^{1}H NMR (two methyl signals at 1.89 and 2.26 ppm) and IR (ν_{CO} at 1922 cm^{-1}) spectral properties similar to those of the ruthenium complex **4**. The structure of **6** has also been determined by X-ray crystallography, and the structure (Figure 2)[10] shows that ligand **3** indeed underwent the same chemical transformation as before (**5**, M = Os) and the osmium complex has composition and stereochemistry similar to those of the ruthenium complex. Complex **6** can also be synthesized using

---

(5) Crystallographic data for **4**: $C_{51}H_{42}N_2O_2P_2Ru$, monoclinic, space group $P2_1/c$, a = 18.1758(7) Å, b = 12.0548(4) Å, c = 20.6448(8) Å, β = 112.663(1)°, V = 4174.1(3) Å^3, Z = 4, λ = 0.71073 Å, R1 = 0.0515, wR2 = 0.1090, GOF = 1.146. Selected distances [Å] and angles [deg]: Ru−C(1), 1.858(3); Ru−C(13), 2.045(3); Ru−N(1), 2.040(2); Ru−O(2), 2.195(2); Ru−P(1), 2.360(8); Ru−P(2), 2.379(8); C(1)−O(1), 1.144(4); N(1)−N(2), 1.280(3); C(2)−O(2), 1.308(4); P(1)−Ru−P(2), 176.88(3); C(13)−Ru−O(2), 154.59(11); C(1)−Ru−N(1), 177.21(13); N(1)−Ru−C(13), 76.75(11); N(1)−Ru−O(2), 77.83(9); O(1)−C(1)−Ru, 178.8(3).

(6) Complex **4** was also synthesized following the same above procedure given in ref 4, using *tert*-butyl alcohol instead of ethanol, and the reflux time was 5 h instead of 3 h. Yield: 45%.

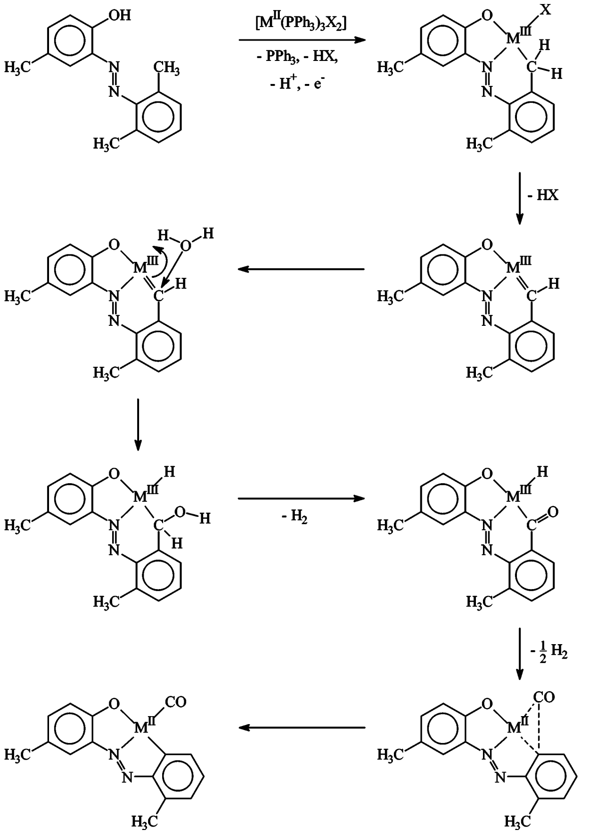
(7) Complex **4** was also synthesized following the same above procedure given in ref 4, using benzene instead of ethanol. Yield: 57%.

(8) Acharyya, R.; Peng, S. M.; Lee, G. H.; Bhattacharya, S. Unpublished results.

(9) Complex **6**: This complex was synthesized by following the same above procedure as for complex **4**, using 2-methoxyethanol instead of ethanol and [Os$(PPh_3)_3Br_2$] instead of [Ru$(PPh_3)_3Cl_2$]. The reflux time was 7 h instead of 3 h. Yield: 32%. Calcd: C, 63.35%; H, 4.35%; N, 2.90%. Found: C, 63.07%; H, 4.33%; N, 2.98%. ^{1}H NMR: 1.89 (CH_3); 2.26 (CH_3); 6.01 (d, 1H, J = 8.5); 6.06 (s, 1H); 6.24 (t, 1H, J = 7.6); 6.31 (d, 1H, J = 7.6); 6.38 (d, 1H, J = 8.4); 6.96 (d, 1H, J = 8.5); 7.13−7.40 ($2PPh_3$). ^{13}C NMR: 127.90, 129.98, 133.91 and 134.57 ($2PPh_3$); 19.29 (CH_3); 19.95 (CH_3); 117.80; 120.04; 121.73; 121.84; 129.98; 130.52; 133.70; 134.13; 135.35; 138.50; 143.37; 166.13 (Ru−C (Ar)); 175.06 (CO). ^{31}P NMR: 46.73(s).

(10) Crystallographic data for **6**: $C_{51}H_{42}N_2O_2P_2Os$, monoclinic, space group $P2_1/c$, a = 18.2014(1) Å, b = 12.0662(1) Å, c = 20.6995(2) Å, β = 112.7269(4)°, V = 4193.09(6) Å^3, Z = 4, λ = 0.71073 Å, R1 = 0.0377, wR2 = 0.0785, GOF = 1.083. Selected distances [Å] and angles [deg]: Os−C(1), 1.874(6); Os−C(13), 2.059(5); Os−N(1), 2.062(4); Os−O(2), 2.206(3); Os−P(1), 2.365(12); Os−P(2), 2.376(12); C(1)−O(1), 1.117(6); N(1)−N(2), 1.288(5); C(2)−O(2), 1.304(5); P(1)−Os−P(2), 177.15(4); C(13)−Os−O(2), 153.16(17); C(1)−Os−N(1), 177.55(18); N(1)−Os−C(13), 76.17(18); N(1)−Os−O(2), 77.00(13); O(1)−C(1)−Os, 179.2(6).

Scheme 1. Probable Steps in the Formation of Complexes **4** and **6**[13]



tert-butyl alcohol or benzene as solvent instead of 2-methoxyethanol.[11,12] Reaction of ligand **7** with $[Os(PPh_3)_3Br_2]$ in refluxing 2-methoxyethanol in the presence of triethylamine has also afforded a cyclometalated complex of osmium(III) (**8**; M = Os, X = Br).[8] These results again show that it is the displaced methyl group of ligand **3**, not 2-methoxyethanol, which was the source of CO in complex **6**.

Mechanism of the observed chemical transformation of **3** is not completely clear to us. However, the speculated sequences illustrated in Scheme 1 seem probable.[13] In the initial step, ligand **3** coordinates to the metal center as a tridentate C,N,O-donor via loss of the phenolic proton and another proton from one methyl group in the arylazo fragment. This particular coordination mode of ligand **3** has been observed by us in some other complexes,[2i] and such C−H activation has also been reported by many others.[14] In this $CNOP_2X$ coordination environment the bivalent metal gets oxidized to the trivalent state,[2h,3] and the metalated CH_2 fragment undergoes further C−H activation, via loss of HX, affording a reactive carbene species. Upon reaction with water (present in the commercial solvent as well as in triethylamine) the M═C−H fragment gets converted into a M(H)−C═O fragment via elimination of hydrogen. Reductive elimination of hydride, followed by migration of the CO fragment, yields the carbonyl complex of the bivalent metals. Similar metal-assisted C−C bond activation is well documented in the literature.[15]

The present study shows that C−H activation of selective alkyl groups, linked to the ortho carbon of the phenyl ring in the arylazo fragment of **1**, may be easily achievable by reaction of such ligands with the $[M(PPh_3)_3X_2]$ (M = Ru, Os; X = Cl, Br) complexes, leading to the formation of interesting cyclometalated complexes. Such possibilities are currently under exploration.

Acknowledgment. Financial assistance received from the Department of Science and Technology, New Delhi [Grant No. SP/S1/F33/98], the Council of Scientific and Industrial Research, New Delhi [Grant No. 01(1675)/00/EMR-II], and the University Grants Commission, New Delhi [Grant No. F.12-56/2001(SR-I)], is gratefully acknowledged. The authors thank Dr. Falguni Basuli for useful discussions.

Supporting Information Available: Crystallographic details for **4** and **6** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC034968I

---

(11) Complex **6** was also synthesized following the same above procedure given in ref 9, using *tert*-butyl alcohol instead of 2-methoxyethanol, and the reflux time was 11 h instead of 7 h. Yield: 39%.

(12) Complex **6** was also synthesized following the same above procedure given in ref 9, using benzene instead of 2-methoxyethanol. Yield: 46%.

(13) The two axially coordinated PPh_3 ligands are not shown for clarity.

(14) (a) Arndtsen, B. A.; Bergman, R. G.; Mobley, T. A.; Patertson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154. (b) Hall, C.; Perutz, R. N. *Chem. Rev.* **1996**, *96*, 3125. (c) Shilov, A. E.; Shul'pin, G. B. *Chem. Rev.* **1997**, *97*, 2879. (d) Martin, R. L. *J. Am. Chem. Soc.* **1999**, *121*, 9459. (e) Crabtree, R. H. *J. Chem. Soc., Dalton Trans.* **2001**, 2437. (f) Labinger, J. A.; Bercaw, J. E. *Nature* **2002**, *417*, 507. (g) Iron, M. A.; Lo, H. C.; Martin, J. M. L.; Keinan, E. *J. Am. Chem. Soc.* **2002**, *124*, 7041. (h) Hagen, H.; Boersma, J.; van Koten, G. *Chem. Soc. Rev.* **2002**, *31*, 357. (i) Bijkstra, H. P.; Albrecht, M.; van Koten, G. *Chem. Commun.* **2002**, 126. (j) Rybtchinski, B.; Cohen, R.; Ben-David, Y.; Martin, J. M. L.; Milstein, D. *J. Am. Chem. Soc.* **2003**, *125*, 11041.

(15) (a) van der Boom, M. E.; Kraatz, H. B.; Hassner, L.; Ben-David, Y.; Milstein, D. *Organometallics* **1999**, *18*, 3873. (b) Sundermann, A.; Ujan, O.; Milstein, D.; Martin, J. M. L. *J. Am. Chem. Soc.* **2000**, *122*, 7095. (c) Cohen, R.; van der Boom, M. E.; Shimon, L. J. W.; Milstein, D. *J. Am. Chem. Soc.* **2000**, *122*, 7723. (d) Cao, Z.; Hall, M. B. *Organometallics* **2000**, *19*, 3338. (e) Coalter, J. N.; Huffman, J. C.; Caulton, K. G. *Organometallics* **2000**, *19*, 3569. (f) Rybtchinski, B.; Oevers, S.; Montag, M.; Vigalok, A.; Rozenberg, H.; Martin, J. M. L.; Milstein, D. *J. Am. Chem. Soc.* **2001**, *123*, 9064. (g) Gauvin, R. M.; Rozenberg, H.; Shimon, L. J. W.; Milstein, D. *Organometallics* **2001**, *20*, 1719. (h) Meijer, M. D.; van Klink, G. P. M.; van Koten, G. *Coord. Chem. Rev.* **2002**, *230*, 141.