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Communication

# Unprecedented Migration of a Methyl Group in 2-(2′,6′-Dimethylphenylazo)-4-methylphenol Mediated by Ruthenium

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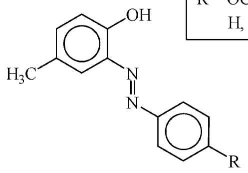
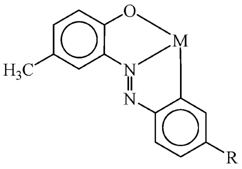
An unprecedented chemical transformation of 2-(2′,6′-dimethylphenylazo)-4-methylphenol has been observed upon its reaction with [$Ru(PPh_3)_2(CO)_2Cl_2$] whereby the methyl group at the 2′ position migrates to the 4′ or 6′ position.



R = $OCH_3$, $CH_3$, H, Cl, $NO_2$

**1**



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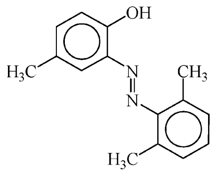

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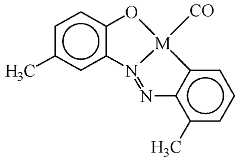

**4**

The present work has emerged from our interest in the C−H and C−C activation of 2-(arylazo)phenols (**1**) and related ligands.[1] While ligand **1** has been observed to undergo C−H activation at one ortho position of the phenyl ring in the arylazo fragment leading to the formation of cyclometalated species (**2**),[1a,c−k,2] we have recently observed that a modified 2-(arylazo)phenol, viz. 2-(2′,6′-dimethylphenylazo)-4-methylphenol (**3**), in which both the ortho positions of the phenyl ring in the arylazo fragment are strategically blocked by methyl groups, displays interestingly different reactivity.[1b] Upon its reaction with [$Ru(PPh_3)_3Cl_2$], or its osmium analogue, ligand **3** has been observed to undergo an unusual chemical transformation, whereby one methyl group from the phenyl ring of the arylazo fragment migrates to the metal center via oxidation to CO (**4**). Susceptibility of the metal center toward oxidation to the +3 state was speculated to play the key role in the observed oxidative migration of the methyl group.[1b] This has encouraged us to explore the reactivity of ligand **3** with other platinum metal complexes where the metal center is not so easily oxidizable, and thus, [$Ru(PPh_3)_2(CO)_2Cl_2$] has been selected as the ruthenium complex in the present study. The presence of strong $\pi$-acid CO, in addition to $PPh_3$, in the coordination sphere makes the metal center in [$Ru(PPh_3)_2(CO)_2Cl_2$] much less oxidizable relative to that in [$Ru(PPh_3)_3Cl_2$]. It may be mentioned here that reactivity of [$Ru(PPh_3)_3Cl_2$] and [$Ru(PPh_3)_2(CO)_2Cl_2$] toward a particular organic ligand has been found to be significantly different.[3] Herein, we wish to report an interesting migration of a methyl group in ligand **3** that took place upon its reaction with [$Ru(PPh_3)_2(CO)_2Cl_2$].

Reaction of ligand **3** with [$Ru(PPh_3)_2(CO)_2Cl_2$] was carried out in refluxing 2-methoxyethanol in the presence of triethylamine, which afforded two green complexes **5** and **6**, which were separated by chromatography.[4,5] The green band of complex **5** separated first followed by that of complex **6**. Though ligand **3** contains three methyl groups, the $^1$H NMR spectrum of complex **5** showed a single aromatic methyl signal at 2.31 ppm. Besides that, a triplet (3H) and a quartet (2H) were observed at 1.15 and 1.44 ppm, respectively, the origin of which was initially not clear. In complex **6**, three methyl signals were observed at 1.25, 1.83, and 2.30 ppm.

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However, three singlets (1H each) were observed in the aromatic region at 6.05, 6.11, and 6.52 ppm, the origin of which was again not clear. The $^1$H NMR spectral data of complexes **5** and **6** thus indicate that ligand **3** has probably undergone some unexpected chemical transformations during its reaction with [Ru(PPh$_3$)$_2$(CO)$_2$Cl$_2$]. To verify this speculation, identity of both the complexes **5** and **6** has been unveiled by their structure determination by X-ray crystallography. The structures reveal that the speculation has indeed been correct. The structure of complex **5** (Figure 1)[6] shows that one methyl group of ligand **3** has migrated from its original location (say, at the 2′ position) and is inserted (via loss of a proton) into the C−CH$_3$ bond at the 6′ position, thus converting the methyl group (at 6′ position) into an ethyl group. The modified ligand is coordinated to ruthenium as a dianionic tridentate C,N,O-donor. Two PPh$_3$ ligands and a CO are also coordinated to the metal center. Structure of complex **6** (Figure 2)[7] shows that one methyl group of ligand **3** has again migrated from its original location (say at 2′ position); however, it is inserted (via loss of a proton) into the aromatic C−H bond at the 4′ position. Thus, a new methyl group is generated at the 4′ position. The transformed ligand is coordinated to ruthenium as a dianionic tridentate C,N,O-donor. As before, two PPh$_3$ ligands and a CO are also coordinated to the metal center. Complexes **5** and **6** therefore represent examples of two structural isomers.

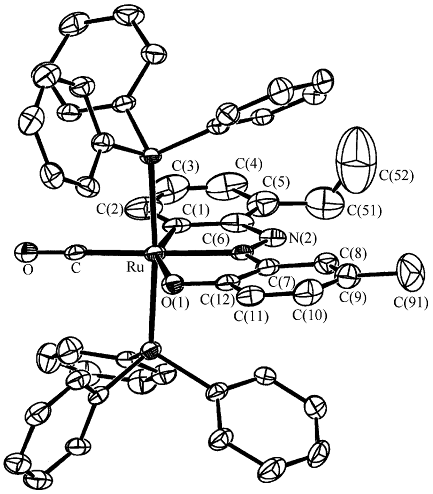

**Figure 1.** Molecular structure of **5**.

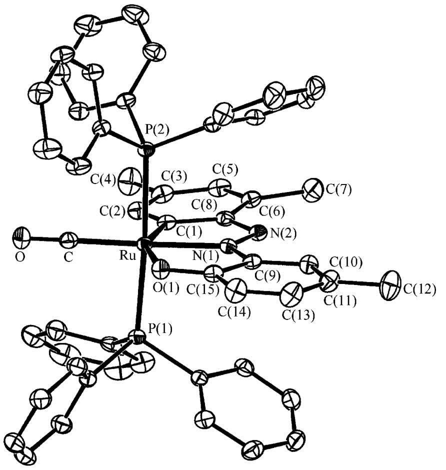

**Figure 2.** Molecular structure of **6**.

To check whether the solvent (2-methoxyethanol) or the base (triethylamine) has served as the source of a methyl or ethyl group, reaction of ligand **3** has been carried out with [Ru(PPh$_3$)$_2$(CO)$_2$Cl$_2$] in toluene and also in benzonitrile using triethylamine, as well as Na$_2$CO$_3$, as base. From each of these reactions, both complex **5** and **6** have been obtained. This clearly indicates that neither the solvent (2-methoxyethanol) nor the base (NEt$_3$) has served as the source of a methyl or ethyl group in the formation of complexes **5** and **6**.

The chemical transformations of ligand **3** observed upon its reaction with [Ru(PPh$_3$)$_2$(CO)$_2$Cl$_2$] are significantly different than that observed upon its reaction with [Ru(PPh$_3$)$_3$Cl$_2$]. However, the present chemical transformations of ligand

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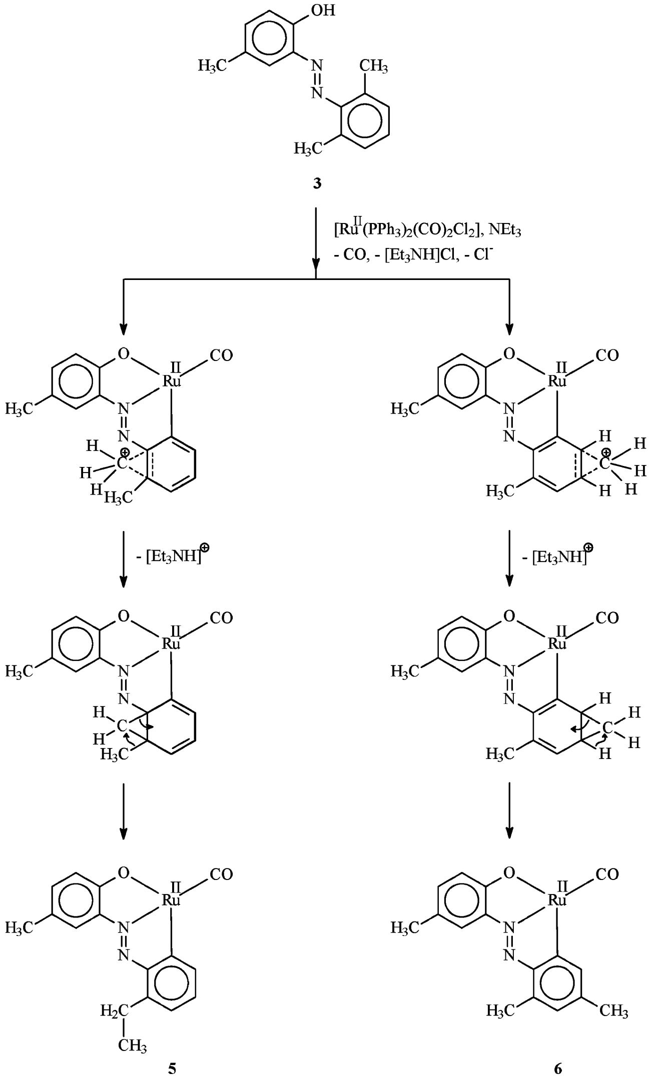
(4) Complexes **5** and **6**: ligand **3** (34 mg, 0.14 mmol) was dissolved in 2-methoxyethanol (40 mL), and to it were added triethylamine (22 mg, 0.24 mmol) and [Ru(PPh$_3$)$_2$(CO)$_2$Cl$_2$] (100 mg, 0.14 mmol). The mixture was then heated at reflux for 24 h to afford a deep brown solution. The 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, two deep green bands (complexes **5** and **6**, respectively) separated, which were extracted with acetonitrile. Upon evaporation of the acetonitrile extracts, complexes **5** and **6** were obtained as crystalline green solids. Yield: 18% (for complex **5**) and 24% (for complex **6**). Calcd: C, 70.03%; H, 4.93%; N, 3.14% (for both the complexes **5** and **6**). Found: C, 70.10%; H, 4.93%; N, 3.19% for complex **5** and C, 70.06%; H, 4.95%; N, 3.18% for complex **6**. Complex **5** $^1$H NMR: 1.15 (CH$_3$, t, $J = 7.5$); 1.44 (CH$_2$, quartet, $J = 7.3$); 2.31 (CH$_3$), 5.92 (d, 1H, $J = 8.3$); 6.06 (s, 1H); 6.33 (d, 1H, $J = 8.3$); 6.81 (d, 1H, $J = 7.2$); 6.85 (d, 1H, $J = 7.2$); 7.14 (t, 1H, $J = 7.5$); 7.17−7.69 (2PPh$_3$). $^{13}$C NMR: 127.90, 129.84, 132.37, and 134.45 (2PPh$_3$); 20.11(CH$_3$); 24.37(CH$_2$); 30.10(CH$_3$); 116.41; 121.02; 124.71; 128.87; 128.97; 132.19; 132.24; 132.47; 132.55; 138.09; 141.10; 164.35 (Ru−C(Ar)); 175.67(CO). $^{31}$P NMR: 50.69(s). Electronic spectral data in dichloromethane solution: ($\lambda$, nm ($\epsilon$, M$^{-1}$ cm$^{-1}$)): 686 (5500), 452 (5500), 436 (6100), 396 (6000), 354 (12 000), 266 (33 500). Cyclic voltammetric data: oxidation$_1$, $E_{1/2} = 0.42$ V, $\Delta E_p = 70$ mV; oxidation$_2$, $E_{pa} = 1.20$ V. Complex **6** $^1$H NMR: 1.25(CH$_3$); 1.83(CH$_3$); 2.30 (CH$_3$); 5.93 (d, 1H, $J = 8.2$); 6.05 (s, 1H); 6.11 (s, 1H); 6.33 (d, 1H, $J = 7.7$); 6.52 (s, 1H); 7.43−7.71 (2PPh$_3$). $^{13}$C NMR: 127.84, 129.76, 132.26, and 134.49 (2PPh$_3$); 19.44 (CH$_3$); 21.70 (CH$_2$); 30.10 (CH$_3$); 116.45; 121.20; 124.23; 128.86; 128.96; 132.08; 132.33; 132.44; 132.56; 138.10; 140.77; 163.36 ((Ru−C(Ar)); 175.89 (CO). $^{31}$P NMR: 50.75(s). Electronic spectral data in dichloromethane solution: ($\lambda$, nm ($\epsilon$, M$^{-1}$ cm$^{-1}$)): 686 (5400), 450 (5100), 432 (5800), 396 (6500), 356 (11 100), 268 (27 500). Cyclic voltammetric data: oxidation$_1$ $E_{1/2} = 0.40$ V, $\Delta E_p = 70$ mV; oxidation$_2$, $E_{pa} = 1.00$ V.

(5) A $^1$H NMR spectrum of the reaction mixture, prior to separation of complexes **5** and **6** by chromatography on silica, has been recorded. The spectrum looks complicated, because of the presence of other species; however, it clearly indicates the presence of both complex **5** and **6** in the reaction mixture.

(6) Crystallographic data for **5**. C$_{52}$H$_{44}$N$_2$O$_2$P$_2$Ru, monoclinic, space group $P2_1/n$, $a = 18.566(8)$ Å, $b = 11.982(4)$ Å, $c = 20.130(10)$ Å, $\beta = 102.239(16)°$, $V = 4376(3)$ Å$^3$, $Z = 4$, $\lambda = 0.710\,73$ Å, R1 = 0.0752, wR2 = 0.1319, GOF = 1.083. Selected distances [Å] and angles [deg]: Ru−C(1), 2.037(5); Ru−C, 1.869(5); Ru−N(1), 2.042(4); Ru−O(1), 2.197(4); Ru−P(1), 2.3633(15); Ru−P(2), 2.3657(15); C(9)−C(91), 1.511(8); C−O, 1.151(6); N(1)−N(2), 1.278(5); C(12)−O(1), 1.308(6); C(5)−C(51), 1.457(10); C(51)−C(52), 1.4994(11); P(1)−Ru−P(2), 174.70(5); C(1)−Ru−O(1), 154.90(18); C−Ru−N(1), 177.3(2); N(1)−Ru−C(1), 77.14(19); N(1)−Ru−O(1), 77.77(15).

(7) Crystallographic data for **6**. C$_{52}$H$_{44}$N$_2$O$_2$P$_2$Ru, monoclinic, space group $P2_1/c$, $a = 18.343(8)$ Å, $b = 12.071(4)$ Å, $c = 20.628(13)$ Å, $\beta = 109.90(2)°$, $V = 4295(4)$ Å$^3$, $Z = 4$, $\lambda = 0.710\,73$ Å, R1 = 0.0325, wR2 = 0.0814, GOF = 1.031. Selected distances [Å] and angles [deg]: Ru−C(1), 2.075(3); Ru−C, 1.875(3); Ru−N(1), 2.056(2); Ru−O(1), 2.229(2); Ru−P(1), 2.3723(10); Ru−P(2), 2.3829(10); C−O, 1.161(3); O(1)−C(15), 1.319(3); N(1)−N(2), 1.301(3); C(3)−C(4), 1.492(5); P(1)−Ru−P(2), 174.91(3); C(1)−Ru−O(1), 154.66(9); C(1)−Ru−N(1), 77.21(10); N(1)−Ru−O(1), 77.45(8).

**Scheme 1.** Probable Steps in the Formation of Complexes **5** and **6**[8]



**3** are again very unusual and, to our knowledge, unprecedented. The mechanism of the observed chemical transformations is not completely clear to us. However, the speculated sequences shown in Scheme 1 seem probable.[8] Upon reaction with $[Ru(PPh_3)_2(CO)_2Cl_2]$, ligand **3** binds to the metal center as a tridentate C,N,O-donor via loss of the phenolic proton and a $CH_3^+$ ion from one ortho position (say, in the 2′ position) in the 2′,6′-dimethylphenylazo fragment. Such metal assisted C−C bond activation is well documented in the literature.[9] The dissociated $CH_3^+$ ion links itself selectively to the electron rich C═C bond within 1′ and 6′ or 3′ and 4′ positions in an $\eta^2$-fashion. Dissociation of a proton from the $\eta^2$-bound $CH_3^+$ ion, followed by usual rearrangements, affords the final complex **5** or **6**.

Electronic spectra of complexes **5** and **6** are found to be similar. Each complex shows several intense absorptions in the visible and ultraviolet regions. The absorptions in the ultraviolet region are believed to be due to transitions within the ligand orbitals, and those in the visible region are attributable to metal-to-ligand charge-transfer transitions. Redox activity of complexes **5** and **6** has been tested by cyclic voltammetry.[10] Both the complexes show two oxidative responses on the positive side of SCE. The first oxidation near 0.4 V is reversible and is assigned to Ru(II)−Ru(III) oxidation. The second oxidation near 1.0 V is irreversible and is tentatively assigned to oxidation of the CNO-coordinated 2-(arylazo)phenolate ligand.

The present study shows that C−C activation of selective alkyl groups, introduced at the ortho position of the phenyl ring in the arylazo fragment of **1**, may be easily achievable by reaction of such ligands with suitable platinum metal complexes. Such possibilities are currently under exploration.

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**Supporting Information Available:** Crystallographic details for complexes **5** and **6** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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

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(10) Cyclic voltammetry was carried out in dichloromethane solution (0.1 M TBAP) at a scan rate of 50 mV $s^{-1}$. $E_{1/2} = 0.5(E_{pa} + E_{pc})$, where $E_{pa}$ and $E_{pc}$ are anodic and cathodic peak potentials respectively; $\Delta E_p = E_{pa} - E_{pc}$.