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5-Bromination of an η^2-8-Quinolyl Ligand Bound to Osmium(II) and Subsequent Lithiation and Derivatization of This Functionalized Ligand[1]

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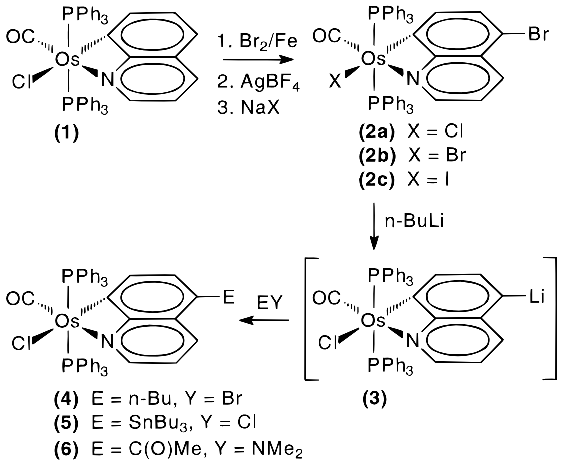
*Summary: Bromination of the 8-quinolyl ligand in the complex Os(η^2-8-quinolyl)Cl(CO)(PPh_3)$_2$ (**1**) occurs selectively in the 5-position, para to the osmium−carbon bond. Treatment of the brominated product, Os(η^2-8-quinolyl-Br-5)Cl(CO)(PPh_3)$_2$ (**2a**), with BuLi gives an intermediate lithiated quinolyl species Os(η^2-8-quinolyl-Li-5)Cl(CO)(PPh_3)$_2$ (**3**), which undergoes further reactions typical of aryllithium reagents. Treatment with the representative electrophiles n-BuBr, Bu_3SnCl, and $Me_2NC\{O\}Me$ produces Os(η^2-8-quinolyl-Bu-5)Cl(CO)(PPh_3)$_2$ (**4**), Os(η^2-8-quinolyl-$SnBu_3$-5)Cl(CO)(PPh_3)$_2$ (**5**), and Os(η^2-8-quinolyl-C{O}Me-5)Cl(CO)(PPh_3)$_2$ (**6**), respectively. Crystal structures of Os(η^2-8-quinolyl-Br-5)I(CO)(PPh_3)$_2$ (**2b**) and Os(η^2-8-quinolyl-[C{O}Me]-5)Cl(CO)(PPh_3)$_2$ (**6**) have been determined.*

Direct electrophilic substitution of an aryl ligand σ-bound to a transition metal, $L_nM{-}Ar$, is not normally possible because most electrophilic reagents cleave the M−Ar bond rather than substitute the aryl ligand. Nevertheless, we have previously reported successful nitration of aryl ligands bound to ruthenium(II) or osmium(II) using very mild nitrating conditions.[2] In this report we now describe that if the aryl is part of a chelating ligand system such as η^2-8-quinolyl, even bromination using bromine becomes possible without cleavage of the M−Ar bond.

Os(η^2-8-quinolyl)Cl(CO)(PPh_3)$_2$ (**1**) is readily formed by a transmetalation from (8-quinolyl)$_2$Hg to OsHCl(CO)(PPh_3)$_3$.[3] In complex **1** the 8-quinolyl ligand is bound through N and C-8, and the resulting robust four-membered chelate ring persists through many chemical transformations.

The chelated quinolyl group in **1** is selectively brominated in the 5-position and the functionalized ligand is retained bound to osmium (see Scheme 1). The activating and directing properties of the osmium moiety facilitate electrophilic aromatic substitution under mild conditions, and in addition to monobromination, dibromination (**5**, **7**) also occurs.[4] Both nitration (**5**) and dinitration (**5**, **7**) have also been achieved through reaction with copper nitrate/acetic anhydride.[5] In contrast to this observed reactivity of **1** with bromine, an attempted bromination of the related nonchelated naphthyl derivative, Os(1-naphthyl)Cl(CO)(PPh_3)$_2$, resulted only in cleavage of the Os−naphthyl bond.

Scheme 1



The bromination of **1**, when carried out in dichloromethane solvent with 1 equiv of bromine and a catalytic quantity of iron powder, proceeds rapidly at room temperature to give a mixture of Os(η^2-8-quinolyl-Br-5)Cl(CO)(PPh_3)$_2$ (**2a**) and Os(η^2-8-quinolyl-Br-5)Br(CO)(PPh_3)$_2$ (**2b**) in high overall yield.[6] The mixture is easily converted into pure **2a**, **2b**, or Os(η^2-8-quinolyl-Br-5)I(CO)(PPh_3)$_2$ (**2c**) by treatment with $AgBF_4$ followed by addition of the appropriate sodium halide. This bromination reaction of the quinolyl ligand is remarkable because free quinoline undergoes classical bromination only under forcing conditions that result in mixtures of products.[7] To confirm the site of bromination, a crystal structure determination of **2c** was undertaken.[8] The molecular structure is shown in Figure 1. The bond distances between osmium and the brominated quinolyl ligand are not significantly different from the distances found in the parent complex, Os(η^2-8-quinolyl)I(CO)(PPh_3)$_2$.[3] However, the Os−I distance at 2.7082(14) Å is significantly shorter than the corresponding distance of 2.7916(8) Å in Os(η^2-8-quinolyl)I(CO)(PPh_3)$_2$.

Os(η^2-8-quinolyl-Br-5)Cl(CO)(PPh_3)$_2$ (**2a**) can be lithiated by reaction with BuLi in THF to form an intermediate, formulated as Os(η^2-8-quinolyl-Li-5)Cl(CO)(PPh_3)$_2$ (**3**). Although complex **3** was not isolated, this species

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(1) Dedicated to Professor Peter Jutzi on the occasion of his 60th birthday.

(2) Clark, G. R.; Headford, C. E. L.; Roper, W. R.; Wright, L. J.; Yap, V. P. D. *Inorg. Chim. Acta* **1994**, *220,* 261.

(3) Clark, A. M.; Rickard, C. E. F.; Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **1997**, *545*−*546,* 619.

(4) Clark, A. M.; Rickard, C. E. F.; Roper, W. R.; Wright, L. J. Unpublished results.

(5) Nitration of σ-bound phenyl derivatives of ruthenium(II) using the same conditions has been described previously; see ref 2.

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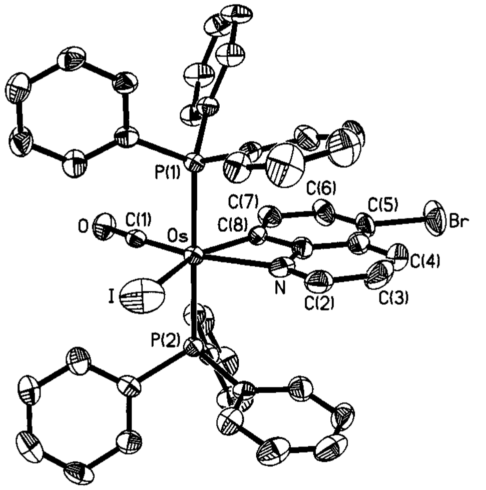

Figure 1. Molecular structure for Os(η^2-8-quinolyl-Br-5)I-(CO)(PPh$_3$)$_2$ (**2c**) (ORTEP, thermal ellipsoids at 50% probability). Selected bond distances (Å) and bond angles (deg): Os−C(1), 1.849(12); Os−C(8), 2.092(10); Os−N, 2.241(10); Os−I, 2.7082(14); C(8)−Os−N, 63.2(4); P(2)−Os−P(1), 175.70(9).

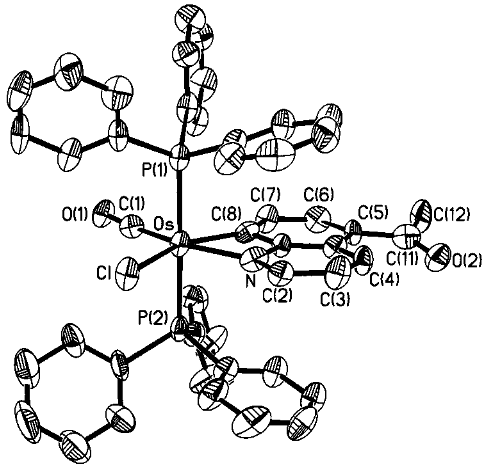

Figure 2. Molecular structure for Os(η^2-8-quinolyl-C{O}-Me-5)Cl(CO)(PPh$_3$)$_2$ (**6**) (ORTEP, thermal ellipsoids at 50% probability). Selected bond distances (Å) and bond angles (deg): Os−C(8), 1.832(15); Os−C(8), 2.077(14); Os−N, 2.196(11); O(2)−C(11), 1.225(17); C(8)−Os−N, 62.8(5); P(2)−Os−P(1), 176.26(13).

generated in situ, when treated with *n*-BuBr, Bu$_3$SnCl, or Me$_2$NC{O}Me, was readily transformed into compounds **4**, **5**, or **6**, respectively, according to Scheme 1.[9] The crystal structure of Os(η^2-8-quinolyl-C{O}Me-5)Cl-(CO)(PPh$_3$)$_2$ (**6**) has been determined,[10] and the molec-

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(6) Synthesis of **2a**−**c**: Os(η^2-8-quinolyl)Cl(CO)(PPh$_3$)$_2$ (**1**) (200 mg, 0.221 mmol) was dissolved in dichloromethane (50 mL), and bromine in the form of pyridine·HBr$_3$ (71 mg, 0.22 mmol), dissolved in methanol (5 mL), was added. Iron powder (2 mg) was added, and the resulting solution was stirred for 1 h. The orange solution was then washed with water in a separating funnel. Because some halide exchange at the metal center occurs during the bromination, the following procedure was adopted to produce pure **2a**, **2b**, and **2c**. The CH$_2$Cl$_2$ solution containing the mixture of **2a** and **2b** obtained as above was stirred with AgBF$_4$ (100 mg) dissolved in water/ethanol (1:1, 10 mL). After 10 min the precipitated AgX was removed by fitration and an excess of NaX (10 equiv) in H$_2$O (20 mL) was added (X = Cl, Br, I for **2a**, **2b**, and **2c**, respectively). This solution was stirred for a further 10 min, then placed on a silica gel chromatography column (10 × 3.5 cm) and eluted using dichloromethane. The first orange band was collected, and crystals were obtained by addition of hexane and reduction of the solvent volume in vacuo to give pure **2a** (178 mg, 82%), **2b** (173 mg, 76%), and **2c** (183 mg, 77%). Data for **2a**−**c**: IR (Nujol mull, cm^{-1}) **2a** 1901 ν(CO), **2b** 1903 ν(CO), **2c** 1903 ν(CO); ^{1}H NMR (400.1 MHz, CDCl$_3$, δ in ppm, TMS at δ 0, *J* in Hz) **2a** 7.14−7.49 (m, 30H, PPh$_3$), 7.07 (d, 1H, *H*2, ^3J(HH) 4.6), 6.48 (dd, 1H, *H*3, ^3J(HH) 4.6, 8.6), 7.72 (d, 1H, *H*4, ^3J(HH) 8.6), 6.93 (d, 1H, *H*6, ^3J(HH) 7.3), 6.78 (d, 1H, *H*7, ^3J(HH) 7.3); **2b** 7.14−7.51 (m, 30H, PPh$_3$), 7.06 (d, 1H, *H*2, ^3J(HH) 4.6), 6.47 (dd, 1H, *H*3, ^3J(HH) 4.6, 8.3), 7.70 (d, 1H, *H*4, ^3J(HH) 8.3), 6.91 (d, 1H, *H*6, ^3J(HH) 7.2), 6.76 (d, 1H, *H*7, ^3J(HH) 7.2); **1c** 7.13−7.55 (m, 30H, PPh$_3$), 7.11 (d, 1H, *H*2, ^3J(HH) 4.5), 6.31 (dd, 1H, *H*3, ^3J(HH) 4.5, 8.6), 7.58 (d, 1H, *H*4, ^3J(HH) 8.6), 6.93 (d, 1H, *H*6, ^3J(HH) 7.1), 6.78 (d, 1H, *H*7, ^3J(HH) 7.1). Anal. Calcd for **2a,** $C_{46}H_{35}BrClNOOsP_2\cdot{}^1/_2CH_2Cl_2$: C, 54.34; H, 3.53; N, 1.36. Found: C, 54.61; H, 3.18; N, 1.47. Anal. Calcd for **2b**, $C_{46}H_{35}Br_2NOOsP_2\cdot CH_2Cl_2$: C, 50.64; H, 3.35; N, 1.26. Found: C, 50.65; H, 3.38; N, 1.22. Anal. Calcd for **2c**, $C_{46}H_{35}BrINOOsP_2$: C, 51.31; H, 3.28; N, 1.30. Found: C, 51.03; H, 3.16; N, 1.20.

(7) Butler, J. L.; Gordon, M. *J. Heterocycl. Chem*. **1975**, *12*, 1015.

(8) Single crystals of **2c** were grown from chloroform/ethanol. Crystal data for **2c**: $C_{46}H_{34}BrINOOsP_2\cdot CHCl_3$, orange plate (0.25 × 0.13 × 0.05 mm), triclinic, space group $P\bar{1}$, $a = 9.0426(1)$ Å, $b = 12.2465(1)$ Å, $c = 20.4051(2)$ Å, $\alpha = 92.0(1)°$, $\beta = 95.746(1)°$, $\gamma = 104.719(2)°$, $V = 2167.72(4)$ Å^3, $Z = 2$, $D_c = 1.831$ g cm^{-3}, $F(000) = 1154$, μ(Mo Kα) = 4.87 mm^{-1}. A total of 21 762 (9600 unique) reflections (1.0° < θ < 28°; area detector, T = 200 K) were measured on a Siemens SMART diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Data were corrected for Lorentz and polarization effects and absorption (SADABS min. and max. corrections 0.375, 0.793). The structure was solved by Patterson methods (SHELXL-97) and difference Fourier techniques and refined by full-matrix least-squares on F^2 (SHELXL-97) to R1 = 0.073 (8125 reflections with $I > 2\sigma(I)$), wR2 = 0.227, S = 1.044. Hydrogen atoms were introduced in calculated positions and allowed to ride on the carrier atom. All non-hydrogen atoms were refined with anisotropic thermal motion. The chloroform solvate shows evidence of disorder, and one chlorine has been split into two half-atoms. Residual density in a final difference Fourier map was +1.16 and −2.17 e Å^{-3}.

(9) Synthesis of **4**, **5**, and **6**: Os(η^2-8-quinolyl-Br-5)Cl(CO)(PPh$_3$)$_2$ (**2a**) (100 mg, 0.102 mmol) was dissolved in dry deoxygenated tetrahydrofuran (10 mL). *n*-Butyllithium (1.7 mol L^{-1} in hexanes) was added, under nitrogen (1 equiv for the preparation of **4**, 2 equiv for the preparation of **5** or **6**) at 0 °C, and the flask allowed to warm to room temperature. For **5** or **6** the appropriate reagent was added after 5 min of stirring (4 equiv of Bu$_3$SnCl for **5** or 4 equiv of Me$_2$NC(O)Me for **6**), and the resulting mixture stirred at room temperature for 1 h. For the preparation of **4**, the butyl bromide required as reagent is generated in situ, and to complete the reaction, the solution was allowed to stir for 1 h. Ethanol (10 mL) was added to quench the reaction, and the solution was placed on a silica gel chromatography column (10 × 3.5 cm) and eluted with dichloromethane. The yellow or light orange band was collected, and product obtained by adding ethanol and reducing the solvent volume in vacuo to give pure **4** (27 mg, 28%), **5** (68 mg, 56%), or **6** (31 mg, 32%). Data for **4**: IR (Nujol mull, cm^{-1}) 1893 ν(CO); ^{1}H NMR (400.1 MHz, CDCl$_3$, δ in ppm TMS at δ 0, *J* in Hz) 7.15−7.50 (m, 31H, PPh$_3$ and *H*2), 6.38 (dd, 1H, *H*3, ^3J(HH) 4.6, 8.7), 7.63 (d, 1H, *H*4, ^3J(HH) 8.7), 6.87 (d, 1H, *H*6, ^3J(HH) 7.0) 6.57 (d, 1H, *H*7, ^3J(HH) 7.0), 2.55 (t, 2H, CH_2quinolyl, ^3J(HH) 7.24), 1.41 (m, 2H, CH_2), 1.20 (m, 2H, CH_2), 0.87 (t, 3H, CH_3, ^3J(HH) 7.02). Anal. Calcd for $C_{50}H_{44}ClNOOsP_2\cdot{}^1/_2CH_2Cl_2$: C, 61.35; H, 4.56; N, 1.42. Found: C, 61.70; H, 4.77; N, 1.47C, 61.35; H, 4.56; N, 1.42. Data for **5**: IR 1895 ν(CO); ^{1}H NMR 7.12−7.51 (m, 30H, PPh$_3$), 7.04 (d, 1H, *H*2, ^3J(HH) 4.6), 6.38 (dd, 1H, *H*3, ^3J(HH) 4.6, 8.3), 7.36 (d, 1H, *H*4, ^3J(HH) 8.3), 6.95 (d, 1H, *H*6, ^3J(HH) 6.3), 6.75 (d, 1H, *H*7, ^3J(HH) 6.3), 0.99 (t, 2H, CH_2Sn, ^3J(HH) 8.06), 1.42 (m, 2H, CH_2), 1.24 (m, 2H, CH_2), 0.82 (t, 3H, CH$_3$, ^3J(HH) 7.24). Anal. Calcd for $C_{58}H_{62}ClNOOsP_2Sn$: C, 58.27; H, 5.23; N, 1.17. Found: C, 58.55; H, 4.98; N, 1.35. Data for **6**: IR 1894 ν(CO), 1656 η(acyl); ^{1}H NMR 7.11−7.52 (m, 30H, PPh$_3$), 7.02 (d, 1H, *H*2, ^3J(HH) 4.5), 6.56 (dd, 1H, *H*3, ^3J(HH) 4.5, 8.4), 8.93 (d, 1H, *H*4, ^3J(HH) 8.4), 7.31 (d, 1H, *H*6, ^3J(HH) 7.1), 6.98 (d, 1H, *H*7, ^3J(HH) 7.1), 2.43 (s, 3H, CH_3). Anal. Calcd for $C_{48}H_{38}ClNO_2OsP_2\cdot$THF: C, 61.20; H, 4.54; N, 1.37. Found: C, 61.55; H, 4.78; N, 1.68.

(10) Single crystals of **6** were grown from dichloromethane/ethanol. Crystal data for **6**: $C_{48}H_{38}ClNO_2OsP_2$, yellow prism (0.17 × 0.11 × 0.08 mm), monoclinic, space group $P2_1/c$, $a = 14.4664(1)$ Å, $b = 17.8919(1)$ Å, $c = 16.9623(2)$ Å, $\beta = 112.499(1)°$, $V = 4056.21(6)$ Å^3, $Z = 4$, $D_c = 1.553$ g cm^{-3}, $F(000) = 1888$, μ(Mo Kα) = 3.33 mm^{-1}. A total of 30 550 (7103 unique) reflections (1.0° < θ < 25°; area detector, T = 200 K) were measured on a Siemens SMART diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Data were corrected for Lorentz and polarization effects and absorption (SADABS min. and max. corrections 0.601, 0.776). The structure was solved by Patterson methods (SHELXL-97) and difference Fourier techniques and refined by full-matrix least-squares on F^2 (SHELXL-97) to R1 = 0.077 (4174 reflections with $I > 2\sigma(I)$), wR2 = 0.188, S = 0.949. Hydrogen atoms were introduced in calculated positions and allowed to ride on the carrier atom. All non-hydrogen atoms were refined with anisotropic thermal motion. Residual density in a final difference Fourier map was +3.62 and −3.16 e Å^{-3}, the residual density being concentrated in the region of the osmium atom.

ular structure is shown in Figure 2. Substitution in the 5-position of the quinolyl group is confirmed. The acetyl group lies in the quinolyl plane, and all bond distances are normal.

The electrophilic aromatic substitution reactions of metalated arenes such as complex **1** promise to be valuable routes to unusually functionalized ligands, and the lithiated intermediate **3**, in particular, allows the introduction of a wide range of functional groups. Some of these substituted products will be valuable building blocks for the construction of more elaborate metalated molecules.

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Supporting Information Available: Tables of crystal data and structure refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for **2c** and **6** (19 pages). See any current masthead page for ordering and Internet access instructions.

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