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Alkyl and Aryl Compounds of Rhodium(III) and Iridium(III) Supported by 4,4′-Di-*tert*-butyl-2,2′-bipyridyl

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Alkylation of $Rh(dtbpy)Cl_3(DMF)$ (**1**) (dtbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridyl, DMF = *N*,*N*-dimethylformamide) with $PhMe_2CCH_2MgCl$ afforded the cyclometalated neophyl compound $\overline{Rh(dtbpy)(CH_2CMe_2C}_6H_4)(CH_2CMe_2Ph)$ (**2**), which reacted with CO to give the adduct $\overline{Rh(dtbpy)(CH_2CMe_2C}_6H_4)(CH_2CMe_2Ph)(CO)$ (**3**). The solid-state structure of **2** shows an agostic interaction between Rh and an ortho phenyl C−H group of the neophyl ligand. Alkylation of **1** with Me_3SiCH_2MgCl gave the dialkyl compound $Rh(dtbpy)(CH_2SiMe_3)_2Cl$ (**4**), which reacted with PPh_3 to give $Rh(dtbpy)(CH_2SiMe_3)_2(Cl)(PPh_3)$ (**5**). Transmetalation of $M(dtbpy)Cl_3(DMF)$ with C_8H_9MgBr (C_8H_9 = 2,5-dimethylphenyl) afforded the triaryl compounds $M(dtbpy)(C_8H_9)_3$ (M = Rh (**6**), Ir (**7**)), which have pseudo-square-pyramidal geometry with one aryl group at the apical position. Reaction of **7** with 2,6-dimethylphenyl isocyanide (xylNC) afforded six-coordinated $Ir(dtbpy)(C_8H_9)_3(xylNC)$ (**8**). The cyclic voltammogram of **7** in CH_2Cl_2 shows a reversible couple at ca. 0.18 V versus ferrocenium−ferrocene that is tentatively assigned as the Ir(IV/III) couple. Treatment of **7** with Ag(OTf) (OTf^- = triflate) in tetrahydrofuran (THF) afforded $[Ir(dtbpy)(C_8H_9)_3\{Ag(OTf)(THF)\}\{Ag_2(OTf)_2\}_3]_\infty$ (**9**), which has a double-chain polymeric structure in the solid state. Transmetalation of $Ir(dtbpy)Cl_3(DMF)$ with $(Ar_F)MgBr$ (Ar_F = 3,5-bis(trifluoromethyl)phenyl) afforded the mono-aryl compound $Ir(dtbpy)(Ar_F)(DMF)Cl_{1.4}Br_{0.6}$ (**10**), which reacted with xylNC to give $Ir(dtbpy)(Ar_F)(DMF)Cl_{1.4}Br_{0.6}(xylNC)$ (**11**). The crystal structures of **2**, **6**−**9**, and **11** have been determined.

Introduction

Transition metal complexes containing 2,2′-bipyridyl (bpy) and related ligands are of significance due to their interesting redox and photoluminescent properites[1,2] and their use as building blocks in supramolecular chemistry.[3] Our interest in the organometallic chemistry of bpy compounds is stimulated by the reports that organoiridium compounds in conjunction with chelating ligands, notably 2,2′-bipyridyl (bpy), can catalyze selective borylation[4,5] and silylation[6] of arenes under mild conditions. Among catalysts studied, iridium compounds containing electron-rich 4,4′-di-*tert*-butyl-2,2′-bipyridyl (dtbpy) were found to be most active in the arene borylation. It is believed that the active species of the Ir-catalyzed borylation are Ir boryl compounds[7] that can activate arene C−H bonds, presumably via Ir(V) aryl intermediates.[8] Understanding of organometallic chemistry of Ir(bpy) σ-alkyl and -aryl compounds will help design new Ir-based catalysts for C−H activation and functionalization. To this end, we set out to synthesize Ir and Rh bpy compounds containing σ-alkyl and -aryl ligands and explore their reaction chemistry.

Rh(III) and Ir(III) compounds containing three or more σ-alkyl or -aryl ligands are rather uncommon. Examples include the homoleptic alkyls (e.g., $[Li(TMEDA)]_3[M(Me)_6]$, where M = Ir, Rh; TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine)[9] and aryls (e.g., $M(mes)_3$, $Ir(mes)_4$, where mes = 2,4,6-

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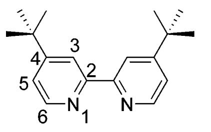
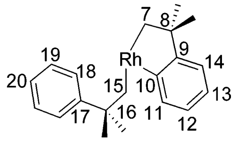
trimethylphenyl,[10] Rh(C$_6$Cl$_5$)$_3$,[11] and [Rh(C$_6$Cl$_5$)$_4$]$^-$,[12]), pentamethylcyclopentadienyl alkyls (e.g., Cp*MMe$_4$), and oxo alkyls/aryls (e.g., [Rh(CH$_2$CMe$_3$)$_3$]$_2$(μ-O),[13] Ir(mes)$_3$O,[14] and [Ir(mes)$_3$]$_2$(μ-O)).[14,15] While Rh(III) trialkyl compounds supported by chelating amine ligands such as Rh(R′$_3$TACN)R$_3$ (R′ = H, Me; R = Me or Et; TACN = 1,4,7-triazacyclononane)[16] and Rh(TMEDA)(C$_4$H$_8$S)Me$_3$[13] are known, analogous alkyl/aryl compounds containing bpy have not been synthesized.

Recently, we studied the transmetalation of Ir(dtbpy)Cl$_3$(DMF) (DMF = *N*,*N*-dimethyformamide) with Grignard reagents. We found that alkylation of Ir(dtbpy)Cl$_3$(DMF) with Me$_3$SiCH$_2$MgCl led to C−Si cleavage of the alkyl group and formation of a Ir(III) silyl alkyl compound, whereas that with PhMe$_2$CCH$_2$MgCl resulted in an iridacycle, illustrating some interesting organometallic chemistry of the Ir^{III}bpy core.[18] Herein, we describe the synthesis and crystal structures of a dtbpy-supported rhodacycle as well as Rh(III) and Ir(III) triaryl compounds. The isolation of an Ir/Ag polymeric compound, in which the Ag(I) ions bind to the Ir-bound aryl ligands in an η^2-fashion, will also be reported.

Experimental Section

General Considerations. All manipulations were carried out under nitrogen by standard Schlenk techniques. Solvents were purified, distilled, and degassed prior to use. NMR spectra were recorded on a Varian Mercury 300 spectrometer operating at 300, 121.5, and 282.4 MHz for ^{1}H, ^{31}P, and ^{19}F, respectively. Chemical shifts (δ, ppm) were reported with reference to SiMe$_4$ (^{1}H and ^{13}C), P(OMe)$_3$ (^{31}P), and C$_6$H$_5$CF$_3$ (^{19}F). Infrared spectra were recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer; mass spectra, on a Finnigan TSQ 7000 spectrometer. Cyclic voltammetry was performed with a Princeton Applied Research (PAR) model 273A potentiostat. The working and reference electrodes were glassy carbon and Ag/AgNO$_3$ (0.1 M in acetonitrile) electrodes, respectively. Potentials were reported with reference to the ferrocenium−ferrocene (Cp$_2$Fe$^{+/0}$). Elemental analyses were performed by Medac Ltd., Surrey, UK. The ligand 4,4′-di-*tert*-butyl-2,2′-bipyridyl (dtbpy) was obtained from Aldrich and used as received. [Ir(dtbpy)Cl$_3$(DMF)] (DMF = *N*,*N*-dimethylformamide) was prepared by treatment of IrCl$_3$ with dtbpy in refluxing DMF as described elsewhere.[18] Atom-labeling schemes for the dtbpy ligand and rhodacyclic neophyl compounds are shown below.





Preparation of Rh(dtbpy)Cl$_3$(DMF) (1). To a solution of RhCl$_3$·*x*H$_2$O (100 mg) in DMF (2 mL) was added dtbpy (138 mg, 0.515 mmol), and the mixture was heated at reflux for 3 h. To the cooled mixture was added Et$_2$O (20 mL), and the yellow precipitate was collected, washed with Et$_2$O, and air-dried. Yield: 195 mg (69%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.44 (s, 9H, *t*-Bu), 1.47 (s, 9H, *t*-Bu), 3.18 (s, 3H, N*Me*$_2$), 3.23 (s, 3H, N*Me*$_2$), 7.55 (dd, *J* = 6.0, 2.1 Hz, 1H, H^5), 7.66 (dd, *J* = 6.0, 2.0 Hz, 1H, H^5), 7.96 (d, *J* = 2.1 Hz, 1H, H^3), 8.03 (d, *J* = 2.0 Hz, 1H, H^3), 8.67 (s, 1H, C*H*O), 8.98 (d, *J* = 6.0 Hz, 1H, H^6), 9.82 (d, *J* = 6.6 Hz, 1H, H^6). MS (FAB): *m*/*z* 478.1 (M$^+$ + 1 − DMF). Anal. Calcd for C$_{21}$H$_{31}$Cl$_3$N$_3$ORh·0.5Et$_2$O: C, 47.0; H, 6.1; N, 7.1. Found: C, 47.2; H, 6.1; N, 7.3.

Preparation of Rh(dtbpy)(CH$_2$CMe$_2$C$_6$H$_4$)(CH$_2$CMe$_2$Ph) (2). To a suspension of **1** (100 mg, 0.182 mmol) in THF (25 mL) was added PhMe$_2$CCH$_2$MgCl (0.91 mL of a 0.8 M solution in THF, 0.726 mmol) at −78 °C. The mixture was stirred at this temperature for 1 h, warmed to room temperature, and stirred overnight. The volatiles were removed in vacuo, and the residue was extracted with hexane. The extracts were concentrated and cooled at −40 °C to give orange crystals that were suitable for X-ray diffraction analysis. Yield: 88 mg (76%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.81 (s, 3H, Me), 1.18 (s, 3H, Me), 1.22 (s, 3H, Me), 1.39 (s, 18H, *t*-Bu), 1.57 (s, 3H, Me), 1.89 (dd, *J* = 8.1, 3.2 Hz, 1H, H^7), 6.38 (t, *J* = 7.6 Hz, 1H, H^{20}), 6.61 (t, *J* = 7.6 Hz, 2H, H^{19}), 6.79 (d, *J* = 7.9 Hz, 1H, H^{14}), 6.83 (d, *J* = 7.6 Hz, 2H, H^5), 6.90−6.99 (m, 2H, H^{12,13}), 7.20 (s, 1H, H^3), 7.23 (s, 1H, H^3), 7.78 (d, *J* = 6.7 Hz, 2H, H^6), 7.87 (d, *J* = 1.8 Hz, 1H, H^{11}), 8.27 (broad, 1H, H^{18}), 8.36 (broad, 1H, H$^{18'}$). Resonances for the methylene protons H^{15}, H^{17}, and H$^{17'}$ were found to be hidden by intense peaks in the δ 1−2 ppm region but could be located at δ 1.31 (H^{15}), 1.43 (H^7), and 1.78 (H$^{15'}$) by means of a ^{1}H,^{1}H COSY experiment. MS (FAB): *m*/*z* 637.2 (M$^+$ + 1). Anal. Calcd for C$_{38}$H$_{49}$N$_2$Rh: C, 71.7; H, 7.8; N, 4.4. Found: C, 72.2; H, 7.9; N, 4.3.

Preparation of Rh(dtbpy)(CH$_2$CMe$_2$C$_6$H$_4$)(CH$_2$CMe$_2$Ph)(CO) (3). Carbon monoxide was bubbled into a solution of **2** (50 mg, 0.079 mmol) in CH$_2$Cl$_2$ (25 mL) at 0 °C for 30 s. The mixture was warmed at room temperature and stirred for 4 h. The volatiles were removed in vacuo, and the residue was recrystallized from hexane at −40 °C to give a yellow powder. Yield: 45 mg, 86%. IR (KBr, cm^{-1}): 1987 (ν_{CO}). ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 0.88 (s, 9H, *t*-Bu), 0.99 (s, 9H, *t*-Bu), 1.05 (s, 3H, Me), 1.74 (s, 3H, Me), 1.85 (s, 3H, Me), 1.93 (s, 3H, Me), 2.17 (d, *J* = 10.9 Hz, 1H, H^{15}), 2.20 (d, *J* = 4.0 Hz, 1H, H^7), 2.26 (d, *J* = 4.0 Hz, 1H, H^7), 3.19 (d, *J* = 10.9 Hz, 1H, H^{15}), 6.15 (dd, *J* = 5.7, 1.8 Hz, 1H, H^5), 6.70 (dd, *J* = 5.7, 1.8 Hz, 1H, H^5), 7.02 (dd, *J* = 7.5, 6.0 Hz, 1H, H^{14}), 7.23−7.33 (m, 5H, H^{12,13} and H^{19,20}), 7.63 (s, 1H, H^3), 7.71 (s, 1H, H^3), 7.77 (d, *J* = 8.4 Hz, 2H, H^{18}), 7.95 (dd, *J* = 7.2, 1.8 Hz, 1H, H^{11}), 8.21 (d, *J* = 5.7 Hz, 1H, H^6), 8.73 (d, *J* = 5.7 Hz, 1H, H^6). MS (FAB): *m*/*z* 665.3 (M$^+$ + 1). Anal. Calcd for C$_{39}$H$_{49}$N$_2$ORh·0.5H$_2$O: C, 69.5; H, 7.5; N, 4.2. Found: C, 69.5; H, 7.5; N, 3.9.

Preparation of Rh(dtbpy)(CH$_2$SiMe$_3$)$_2$Cl (4). To a suspension of **1** (100 mg, 0.182 mmol) in THF (25 mL) was added Me$_3$SiCH$_2$MgCl (0.91 mL of a 0.8 M solution in THF, 0.726 mmol) at −78 °C. The mixture was slowly warmed to room temperature and stirred overnight. The volatiles were removed in vacuo, and the residue was extracted with hexane. Concentration and cooling at −40 °C gave orange crystals. Yield: 84 mg (79%). ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 0.31 (s, 18H, CH$_2$Si*Me*$_3$), 0.75 (d, *J* = 11.4 Hz, 2H, C*H*$_2$SiMe$_3$), 0.92 (s, 9H, *t*-Bu), 0.95 (s, 9H, *t*-Bu), 2.14 (d, *J*

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= 11.4 Hz, 2H, CH_2SiMe$_3$), 6.65 (d, *J* = 5.5 Hz, 1H, H^5), 6.85 (d, *J* = 6.0 Hz, 1H, H^5), 7.65 (s, 1H, H^3), 7.85 (s, 1H, H^3), 8.81 (d, *J* = 6.0 Hz, 1H, H^6), 10.04 (d, *J* = 5.5 Hz, 1H, H^6). Anal. Calcd for $C_{26}H_{46}ClN_2RhSi_2 \cdot H_2O$: C, 52.1; H, 8.1; N, 4.7. Found: C, 52.4; H, 8.0; N, 4.7.

Preparations of M(dtbpy)(C_8H_9)$_3$ (C_8H_9 = 2,5-dimethylphenyl) (M = Rh (6), Ir (7)). To a suspension of M(dtbpy)Cl$_3$(DMF) (100 mg) in THF (25 mL) was added ca. 3 equiv of C_8H_9MgBr (0.78 mL of a 0.8 solution of THF, 0.625 mmol) at −78 °C. The mixture was slowly warmed to room temperature and stirred overnight. The volatiles were removed in vacuo, and the residue was extracted with hexane. Concentration and cooling at −40 °C afforded orange (**6**) or brown (**7**) crystals, which were further recrystallized from CH_2Cl_2/hexane. X-ray quality crystals were grown from solutions of hexane or benzene/hexane.

6: Yield: 82 mg (66%). ^{1}H NMR (300 MHz, C_6D_6): δ 0.65 (s, 18H, *t*-Bu), δ 1.77−2.14 (overlapping s, 18H, Me), 6.21−7.42 (m, 15H, aromatic protons). MS (FAB): *m*/*z* 687.3 (M$^+$ + 1). Anal. Calcd for $C_{42}H_{51}N_2Rh \cdot CH_2Cl_2$: C, 66.9; H, 6.9; N, 3.6. Found: C, 66.4; H, 7.6; N, 3.1.

7: Yield: 75 mg (62%). ^{1}H NMR (300 MHz, C_6D_6): δ 0.92 (s, 18H, *t*-Bu), 2.15−2.40 (overlapping s, 18H, Me), 6.47−6.51 (m, 3H, aromatic protons), 6.97−7.13 (m, 8H, aromatic protons), 7.33 (s, 1H, H^3), 7.37 (s, 1H, H^3), 7.54 (d, *J* = 5.7 Hz, 2H, H^6). MS (FAB): *m*/*z* 776.3 (M$^+$). Anal. Calcd for $C_{42}H_{51}IrN_2 \cdot 1/2C_6H_{14}$: C, 66.0; H, 7.1; N, 3.4. Found: C, 66.2; H, 7.0; N, 3.1.

Preparation of Ir(dtbpy)(C_8H_9)$_3$(xylNC) (xyl = 2,6-dimethylphenyl) (8). To a solution of **7** (50 mg, 0.064 mmol) in CH_2Cl_2 (25 mL) was added 2,6-dimethylphenylisocyanide (8.5 mg, 0.065 mmol), and the mixture was stirred at room temperature overnight. The volatiles were removed in vacuo, and the residue was rinsed with hexane and further recrystallized from THF/hexane to give red single crystals. Yield: 45 mg (78%). IR (KBr, cm^{-1}): 2091 (ν_{CN}). ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.45 (s, 18H, *t*-Bu), 1.55 (s, 3H, Me), 1.86 (s, 3H, Me), 1.90−2.38 (overlapping s, 18H, Me), 6.41 (s, 2H, H^3), 6.62−6.75 (m, 9H, aromatic protons), 6.87 (d, *J* = 7.5 Hz, 2H, H_m of xyl), 6.96 (t, 7.5 Hz, 1H, H_p of xyl), 7.43 (d, *J* = 5.7 Hz, 2H, H^5), 7.89 (d, *J* = 5.7 Hz, 2H, H^6). MS (FAB): *m*/*z* 802.3 (M$^+$ − C_8H_9). Anal. Calcd for $C_{51}H_{60}IrN_3 \cdot C_6H_{14}$: C, 68.9; H, 7.5; N, 4.3. Found: C, 68.8; H, 7.8; N, 4.1

Preparation of [Ir(dtbpy)(C_8H_9)$_3${Ag(OTf)(THF)}{Ag$_2$(OTf)$_2$}]$_\infty$ (OTf$^-$ = triflate) (9). To a solution of **7** (50 mg, 0.064 mmol) in THF (25 mL) was added AgOTf (85 mg, 0.331 mmol), and the mixture was stirred at room temperature for 3 h. The volatiles were removed in vacuo. The residue was washed with hexane and extracted with Et$_2$O. Recrystallization from THF/hexane gave pink crystals. Yield: 69 mg (70%). ^{1}H NMR (300 MHz, C_6D_6): δ 0.98 (s, 9H, *t*-Bu), 1.07 (s, 9H, *t*-Bu), 1.73 (s, 3H, Me), 1.99 (s, 3H, Me), 2.21 (s, 3H, Me), 2.33 (s, 3H, Me), 2.37 (s, 3H, Me), 2.42 (s, 3H, Me), 6.31 (m, 3H, aromatic protons), 6.63 (m, 3H, aromatic protons), 6.87 (s, 2H, aromatic protons), 7.08 (m, 3H, aromatic protons), 7.42 (m, 1H, aromatic proton), 7.51 (m, 1H, aromatic proton), 8.37 (br, 1H, H^6), 8.81 (br, 1H, H^6), all broad peaks. ^{19}F{^{1}H} NMR (C_6D_6): δ −76.6 (s). Anal. Calcd for $C_{45}H_{51}N_2F_9O_9S_3Ag_3Ir \cdot H_2O$: C, 34.5; H, 3.4; N, 1.8. Found: C, 34.3; H, 3.2; N, 1.7. The analytical data indicated the loss of the THF ligand in **9** after recrystallization.

Preparation of Ir(dtbpy)(Ar$_F$)(DMF)Cl$_{1.4}$Br$_{0.6}$ (Ar$_F$ = 3,5-bis(trifluoromethyl)phenyl) (10). To a suspension of Ir(dtbpy)Cl$_3$(DMF) (100 mg, 0.156 mmol) in THF (25 mL) was added Ar$_F$MgBr (0.78 mL of a 0.8 solution of THF, 0.625 mmol) at −78 °C, and the mixture was slowly warmed to room temperature and stirred overnight. The volatiles were removed in vacuo, and the residue was extracted with Et$_2$O. Recrystallization from Et$_2$O/hexane afforded orange crystals. Yield: 97 mg (74%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.46 (s, 18H, *t*-Bu), 2.17 (s, 3H, N*Me*$_2$), 2.20 (s, 3H, N*Me*$_2$), 7.16 (s, 1H, H_p of Ar$_F$), 7.47 (s, 1H, H_o of Ar$_f$), 7.50 (s, 1H, H_o' of Ar$_F$), 7.64 (dd, *J* = 6.3, 2.1 Hz, 2H, H^5), 7.85 (d, *J* = 2.1 Hz, 2H, H^3), 9.84 (d, *J* = 6.3 Hz, 2H, H^6), 10.10 (s, 1H, C*H*O). ^{19}F{^{1}H} NMR (CDCl$_3$): δ −62.14 (s). MS (FAB): *m*/*z* 744 [Ir(dtbpy)(Ar$_f$)Cl$_2$]$^+$, 788 [Ir(dtbpy)(Ar$_f$)(Cl)(Br)]$^+$, 833 [Ir(dtbpy)(Ar$_f$)Br$_2$]$^+$. Anal. Calcd for $C_{29}H_{34}Br_{0.6}Cl_{1.4}F_6IrN_3O$: C, 41.3; H, 4.1; N, 5.0. Found: C, 41.3; H, 4.2; N, 5.0.

Preparation of Ir(dtbpy)(Ar$_F$)(xylNC)Cl$_{1.4}$Br$_{0.6}$ (11). To a solution of **10** (50 mg, 0.059 mmol) in CH_2Cl_2 (25 mL) was added 2,6-dimethylphenyl isocyanide (8 mg, 0.061 mmol), and the mixture was stirred at room temperature overnight. The volatiles were removed in vacuo, and the residue was washed with hexane. Recrystallization from CH_2Cl_2/hexane afforded red crystals suitable for X-ray diffraction analysis. Yield: 48 mg (90%). IR (KBr, cm^{-1}): 2111 (ν_{CN}). ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.45 (s, 18H, *t*-Bu), 2.28 (s, 6H, Me), 7.03 (d, *J* = 7.5 Hz, 2H, H_m of xyl), 7.11 (t, *J* = 8.1 Hz, 1H, H_p of xyl), 7.24 (s, 1H, H_p of Ar$_F$), 7.57 (s, 1H, H_o of Ar$_F$), 7.61 (s, 1H, H_o' of Ar$_F$), 7.65 (d, *J* = 2.1 Hz, 1H, H^5), 7.67 (d, *J* = 2.1 Hz, 1H, H^5), 7.87 (s, 2H, H^3), 9.95 (d, *J* = 6.3 Hz, 1H, H^6), 10.10 (d, *J* = 6.3 Hz, 1H, H^6). ^{19}F{^{1}H} NMR (CDCl$_3$): δ −62.04 (s). MS (FAB): *m*/*z* 840 [Ir(dtbpy)(Ar$_f$)(xylNC)Cl]$^+$, 884 [Ir(dtbpy)(Ar$_f$)(xylNC)Br]$^+$. Anal. Calcd for $C_{35}H_{36}Br_{0.6}Cl_{1.4}F_6IrN_3$: C, 46.6; H, 4.0; N, 4.7. Found: C, 46.9; H, 4.1; N, 4.4.

X-ray Crystallography. Crystallographic data and experimental details for complexes **2**, **6**·1/2C_7H_8, **7**·1/2C_6H_6, **8**·1/2C_6H_{14}·C_4H_8O, **9**·C_4H_8O, and **11** are summarized in Table 1. Intensity data were collected on a Bruker SMART APEX 1000 CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The data were corrected for absorption using the program SADABS.[19] Disorder problems were encountered for *tert*-butyl groups of the dtbpy ligands in some complexes. In **2**, the C12−C14 positions have 65:35 disorder, and those in **6** 35:40:25. In **7**, the C16−C18 positions have 50:50 disorder, whereas in **8**, the C22−C24 and C26−C28 positions are 60:40 and 55:45 disordered, respectively. Carbon atoms of solvent molecules in some complexes were disordered and refined isotropically without hydrogen atoms. Structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL software package.[20] Selected bond lengths and angles for complexes **2**, **6**·1/2C_7H_8, **7**·1/2C_6H_6, **8**·1/2C_6H_{14}·C_4H_8O, **9**·C_4H_8O, and **11** are listed in Tables 2−6, respectively.

Results and Discussion

Cyclometalated Rh(III) Compounds. Alkylation of Rh(dtbpy)Cl$_3$(DMF) (**1**) with a variety of alkylating agents including alkyl lithium and Grignard reagents has been attempted. However, except that with PhMe$_2$CCH$_2$MgCl and Me$_3$SiCH$_2$MgCl, these reactions led to intractable materials that were insoluble in toluene. Treatment of **1** with PhMe$_2$CCH$_2$MgCl afforded the cyclometalated neophyl compound Rh(dtbpy)(CH$_2$CMe$_2$C$_6$H$_4$)(CH$_2$CMe$_2$Ph) (**2**) (Scheme 1). It should be noted that a similar reaction with Ir(dtbpy)Cl$_3$(DMF) gave the 2-*tert*-butylphenyl compound Ir(dtbpy)(CH$_2$CMe$_2$C$_6$H$_4$)(C$_6$H$_4$-*t*-Bu-2) (**D**).[18] While Pd- and Pt-containing metallacycles derived from bis-neopentyl compounds are well-known, to our knowledge, this is the first example of such a rhodacycle supported by a bidentate N-donor ligand. A possible pathway for the formation of **2** is shown in Scheme 1. It is believed that the alkylation of **1** initially gave a trineophyl intermediate **A**. Orthometalation of one neophyl ligand in **A** followed by reductive elimination of *tert*-butylbenzene yielded **2**. On the other hand, alkylation of Ir(dtbpy)Cl$_3$(DMF) gave an unisolated cyclometalated neophyl intermediate **B**, in which the phenyl ring of the iridacycle occupies the apical position.[18] Further cyclometalation of **B** gave an Ir(V) hydride

Table 1. Crystallographic Data and Experimental Details for $\overline{\text{Rh(dtbpy)(CH}_2\text{CMe}_2\text{C}}_6\text{H}_4\text{)}$(CH$_2CMe_2$Ph) (2), Rh(dtbpy)($C_8H_9$)$_3$·1/2$C_7H_8$ (6·1/2C_7H_8), Ir(dtbpy)(C_8H_9)$_3$·1/2C_6H_6 (7·1/2C_6H_6), Ir(dtbpy)(C_8H_9)$_3$(CNxyl)·1/2C_6H_{14}·C_4H_8O (8·1/2C_6H_{14}·C_4H_8O), [Ir(dtbpy)(C_8H_9)$_3${Ag(OTf)(THF)}{$Ag_2(OTf)_2$}]$_\infty$·C_4H_8O (9·C_4H_8O), and Ir(dtbpy)(Ar_F)(DMF)($(Cl_{0.7}Br_{0.3})_2$)(xylNC) (11)

	2	**6**·1/2C_7H_8	**7**·1/2C_6H_6	**8**·1/2C_6H_{14}·C_4H_8O	**9**·C_4H_8O	**11**
formula	$C_{38}H_{49}N_2Rh$	$C_{45.5}H_{55}N_2Rh$	$C_{45}H_{54}IrN_2$	$C_{58}H_{75}IrN_3O$	$C_{53}H_{67}Ag_3F_9$-$IrN_2O_{11}S_3$	$C_{35}H_{36}Br_{0.6}Cl_{1.4}F$-$IrN_{36}$
M_r	636.70	732.83	815.10	1022.41	1691.08	902.44
a, Å	11.244(8)	11.986(9)	11.969(9)	12.855(7)	38.930(12)	9.767(8)
b, Å	11.975(9)	13.717(1)	13.791(1)	17.419(1)	13.750(4)	11.688(1)
c, Å	13.776(1)	13.872(1)	13.868(1)	22.928(1)	22.523(7)	16.293(1)
α, deg	106.461(1)	115.900(1)	115.726(1)	90	90	72.435(1)
β, deg	102.615(1)	106.191(1)	106.275(1)	103.181(1)	92.302(7)	79.732(2)
γ, deg	102.157(1)	91.323(1)	91.496(1)	90	90	86.475(2)
V, Å^3	1661(2)	1942(2)	1950(2)	4999(5)	12047(7)	1744.8(3)
Z	2	2	2	4	8	2
cryst syst	triclinic	triclinic	triclinic	monoclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$C2/c$	$P\bar{1}$
ρ_{calcd}·g × cm^{-3}	1.273	1.253	1.388	1.359	1.865	1.718
T, K	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
μ, mm^{-1}	0.542	0.472	3.455	2.713	3.353	4.682
F(000)	672	774	830	2116	6672	886
no. of reflns	11 271	13 661	12 313	26 797	31 118	11 766
no. of indep reflns	6336	6650	6771	9699	10 539	6720
R_{int}	0.0361	0.0333	0.0265	0.0450	0.1682	0.0321
R_1, wR_2 ($I > 2\sigma(I)$)	0.0452, 0.0813	0.0410, 0.0942	0.0359, 0.0903	0.0413, 0.0930	0.0682, 0.1132	0.0323, 0.0649
R_1, wR_2 (all data)	0.0663, 0.0865	0.0495, 0.0975	0.0422, 0.0927	0.0670, 0.1008	0.0902, 0.1341	0.0449, 0.0675
goodness-of-fit^c	1.005	1.033	1.092	1.009	0.942	0.994

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $\overline{\text{Rh(dtbpy)(CH}_2\text{CMe}_2\text{C}}_6\text{H}_4\text{)}$(CH$_2CMe_2$Ph) (2)

Rh(1)−C(35)	1.997(3)	Rh(1)−C(30)	2.028(3)
Rh(1)−C(20)	2.061(3)	Rh(1)−N(1)	2.154(3)
Rh(1)−N(2)	2.169(2)	Rh(1)−C(25)	2.556(4)
C(35)−Rh(1)−C(30)	82.9(1)	C(35)−Rh(1)−C(20)	94.0(1)
C(30)−Rh(1)−C(20)	89.8(1)	C(35)−Rh(1)−N(1)	93.6(1)
C(30)−Rh(1)−N(1)	91.2(1)	C(20)−Rh(1)−N(1)	172.4(1)
C(35)−Rh(1)−N(2)	167.8(1)	C(30)−Rh(1)−N(2)	90.3(1)
C(20)−Rh(1)−N(2)	96.1(1)	N(1)−Rh(1)−N(2)	76.4(9)
C(35)−Rh(1)−C(25)	103.9(1)	C(30)−Rh(1)−C(25)	167.3(1)
C(20)−Rh(1)−C(25)	79.2(1)	N(1)−Rh(1)−C(25)	98.9(1)
N(2)−Rh(1)−C(25)	84.8(1)		

Table 3. Selected Bond Lengths (Å) and Angles (deg) for M(dtbpy)(C_8H_9)$_3$

	M = Rh (**6**)	M = Ir (**7**)
M−N(1)	2.155(2)	2.138(4)
M−N(2)	2.177(2)	2.139(4)
M−C_{ax}^{a}	2.014(3)	1.988(6)
M−C_{eq}^{b}	2.155(2)	2.026(5)
M−C_{eq}'	2.177(2)	2.041(5)
C_{eq}'−M−C_{eq}	85.9(1)	97.0(2)
C_{eq}'−M−C_{ax}	95.8(1)	96.4(2)
C_{eq}−M−C_{ax}	95.7(1)	87.3(2)
C_{eq}'−M−N(1)	174.1(1)	170.0(2)
C_{eq}−M−N(1)	98.0(1)	99.2(2)
C_{ax}−M−N(1)	88.2(1)	89.9(2)
C_{eq}'−M−N(2)	100.7(1)	97.4(2)
C_{eq}−M−N(2)	169.5(1)	173.6(2)
C_{ax}−M−N(2)	91.6(1)	87.4(2)
N(1)−M−N(2)	74.8(9)	75.6(2)

[a] Carbon atom of the axial aryl group (adjacent the dtbpy ligand). [b] Carbon atom of the equatorial aryl group (opposite the dtbpy ligand).

Table 4. Selected Bond Lengths (Å) and Angles (deg) for [Ir(dtbpy)(C_8H_9)$_3$(CNxyl)] (8)

Ir(1)−C(10)	1.945(5)	Ir(1)−C(41)	2.090(5)
Ir(1)−C(51)	2.094(5)	Ir(1)−N(10)	2.149(4)
Ir(1)−C(31)	2.151(5)	Ir(1)−N(20)	2.166(4)
C(10)−Ir(1)−C(41)	92.1(2)	C(10)−Ir(1)−C(51)	88.1(2)
C(41)−Ir(1)−C(51)	89.9(2)	C(10)−Ir(1)−N(10)	82.9(2)
C(41)−Ir(1)−N(10)	96.5(2)	C(51)−Ir(1)−N(10)	169.1(2)
C(10)−Ir(1)−C(31)	171.5(2)	C(41)−Ir(1)−C(31)	96.2(2)
C(51)−Ir(1)−C(31)	93.7(2)	N(10)−Ir(1)−C(31)	94.3(2)
C(10)−Ir(1)−N(20)	92.5(2)	C(41)−Ir(1)−N(20)	170.5(2)
C(51)−Ir(1)−N(20)	98.5(2)	N(10)−Ir(1)−N(20)	75.9(2)
C(31)−Ir(1)−N(20)	79.0(2)		

Table 5. Selected Bond Lengths (Å) and Angles (deg) for [Ir(dtbpy)(C_8H_9)$_3${Ag(OTf)(THF)}{$Ag_2(OTf)_2$}]$_\infty$ (9)

Ir(1)−C(21)	2.011(12)	Ir(1)−C(41)	2.008(12)
Ir(1)−C(31)	2.030(13)	Ir(1)−N(2)	2.114(11)
Ir(1)−N(1)	2.122(10)	Ag(1)−O(50)	2.378(11)
Ag(1)−O(11)	2.466(11)	Ag(1)−C(26)	2.529(13)
Ag(1)−C(31)	2.568(12)	Ag(1)−C(21)	2.578(12)
Ag(1)−C(36)	2.684(12)	Ag(2)−O(21)	2.269(10)
Ag(2)−C(24)	2.308(13)	Ag(2)−O(31)	2.330(10)
Ag(2)−C(25)	2.582(14)	Ag(3)−O(32)	2.283(10)
Ag(3)−O(23)	2.304(9)	Ag(3)−C(34)^b	2.404(12)
Ag(3)−C(33)^b	2.502(14)	Ag(3)−O(13)^a	2.538(9)
C(21)−Ir(1)−C(41)	98.1(5)	C(21)−Ir(1)−C(31)	87.1(4)
C(41)−Ir(1)−C(31)	92.9(5)	C(21)−Ir(1)−N(2)	172.2(4)
C(41)−Ir(1)−N(2)	87.8(4)	C(31)−Ir(1)−N(2)	97.7(4)
C(21)−Ir(1)−N(1)	98.7(4)	C(41)−Ir(1)−N(1)	92.6(4)
C(31)−Ir(1)−N(1)	171.4(4)	N(2)−Ir(1)−N(1)	75.9(4)

[a] −x, y, −z + $^1/_2$. [b] x + $^1/_2$, y + $^1/_2$, z.

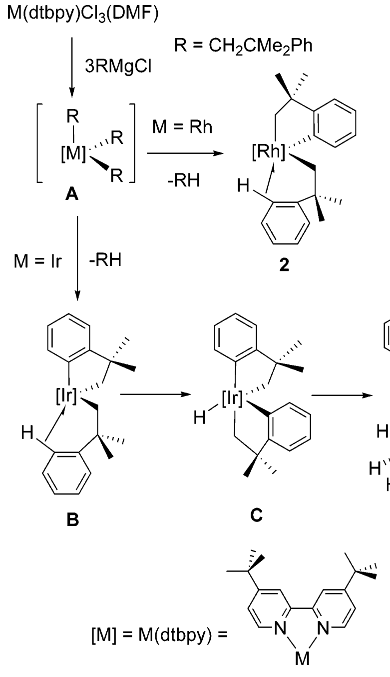
intermediate **C**, which eliminated *tert*-butylbenzene to afford **D**. The difference in outcome between the two alkylations can be attributed to the stronger tendency of Ir to undergo C−H activation compared with Rh.

The ^{1}H NMR spectrum of **2** in $CDCl_3$ at 298 K displays closely spaced resonances in the δ 1−2 ppm region. The singlets at δ 0.81, 1.18, 1.22, and 1.57 ppm are assigned to the methyl protons, and the intense singlet at δ 1.39 ppm is assigned to the *tert*-butyl groups. The resonances of the methylene protons of the rhodacycle (H^7) and one of the two methylene protons of the neophyl ligand (H^{15}) were found to be hidden by the intense peaks in the δ 1−2 ppm region, but could be located at δ 1.31 (H^{15}), 1.43 (H^7), and 1.78 ($H^{15'}$) by means of a ^{1}H,^{1}H COSY experiment. While the two meta phenyl protons of the neophyl ligand (H^{19}) appear as a sharp triplet at δ 6.61 ppm, two overlapping broad resonances were found for the ortho phenyl protons (H^{18}). This suggests that in solution there exists an agostic interaction between Rh and one ortho phenyl C−H group, rendering the two H^{18}'s inequivalent. At lower temperatures (below 280 K), the two resonances sharpened to two doublets at δ 8.20 and 8.37 ppm. When the temperature was

Table 6. Selected Bond Lengths (Å) and Angles (deg) for $\mathrm{Ir(dtbpy)(Ar_F)(xylNC)Cl_{1.4}Br_{0.6}}$ (11)

Ir(1)−C30	2.001(5)	Ir(1)−C(21)	2.068(4)
Ir(1)−N(1)	2.046(3)	Ir(1)−N(2)	2.047(3)
Ir(1)−Cl(2)	2.421(9)	Ir(1)−Cl(1)	2.426(8)
C(30)−Ir(1)−N(1)	95.2(2)	C(30)−Ir(1)−N(2)	93.8(2)
N(1)−Ir(1)−N(2)	79.7(1)	C(30)−Ir(1)−C(21)	174.9(2)
N(1)−Ir(1)−C(21)	88.5(2)	N(2)−Ir(1)−C(21)	88.5(2)
C(30)−Ir(1)−Cl(2)	88.8(1)	N(1)−Ir(1)−Cl(2)	94.9(1)
N(2)−Ir(1)−Cl(2)	174.2(1)	C(21)−Ir(1)−Cl(2)	89.2(2)
C(30)−Ir(1)−Cl(1)	85.8(1)	N(1)−Ir(1)−Cl(1)	175.3(1)
N(2)−Ir(1)−Cl(1)	95.7(1)	C(21)−Ir(1)−Cl(1)	90.5(1)
Cl(2)−Ir(1)−Cl(1)	89.6(3)		

Scheme 1



gradually increased to ca. 303 K, coalescence of the two peaks was observed. At higher temperature (above 320 K), a sharp doublet at δ 8.34 ppm appeared. This result is indicative of a fluxional exchange between the two ortho phenyl protons in solution.

The solid-state structure of **2** is shown in Figure 1; selected bond lengths and angles are listed in Table 2. The geometry around Rh is pseudo-square-pyramidal with the methylene group of the metallacycle occupying the apical position. This is in contrast with the iridacycle **D**, in which the phenyl ring of the metallacycle is at the apical position.[18] An agostic interaction was found between Rh and one ortho phenyl C−H group of the neophyl ligand ($\mathrm{Rh-H_{agostic}} = 2.03(1)$ Å). It may be noted that in **D** an agostic interaction was found between Ir and a *tert*-butyl C−H group.[18] The three Rh−C distances are similar (1.997(3), 2.028(3), and 2.061(3) Å) and compare well with those in $\mathrm{[Rh(bpy)(ppy)_2]^+}$ (ppy = 2-(2-pyridyl)phenyl).[21] The Rh−N distances (av 2.162(2) Å) are longer than those in $\mathrm{[Rh(bpy)(ppy)_2]^+}$ (2.039(3) Å).[21]

Coordinated unsaturated **2** reacted with Lewis bases to give six-coordinated adducts. By contrast, no reactions were found between the iridacycle **D** and Lewis bases[18] presumably due to the steric effect of the bulky 2-*tert*-butylphenyl ligand. Treatment of **2** with CO afforded the adduct $\mathrm{\overline{Rh(dtbpy)(CH_2CMeC_6H_4})(CH_2CMe_2Ph)(CO)}$ (**3**). No migratory insertion of CO to the Rh−C bonds was observed. The IR spectrum of **3** shows an ν_{CO} band at 1987 cm^{-1}, which is similar to that for *fac*-$\mathrm{Rh(TMEDA)(Me)_3(CO)}$ (1978 cm^{-1}).[13] As expected, in the ^{1}H NMR spectrum of **3**, the two ortho phenyl protons H^{18} are equivalent due to the absence of a Rh−H−C agostic interaction and appear as a sharp doublet at δ 7.77 ppm.

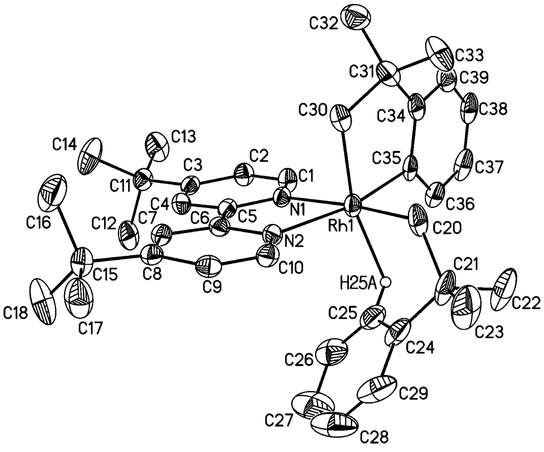
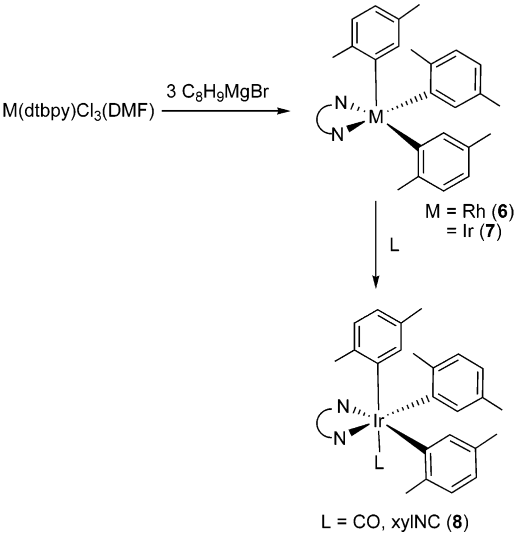


Figure 1. Molecular structure of $\mathrm{\overline{Rh(dtbpy)(CH_2CMe_2C_6H_4})(CH_2CMe_2Ph)}$ (**2**). The ellipsoids are drawn at 40% probability level.

Scheme 2



Rh Trimethylsilylmethyl Compounds. Treatment of **1** with $\mathrm{Me_3SiCH_2MgCl}$ afforded a dialkyl compound characterized as $\mathrm{Rh(dtbpy)(CH_2SiMe_3)_2Cl}$ (**4**), which is probably a dimer. The tris-trimethylsilylmethyl compound could not be isolated even though excess $\mathrm{Me_3SiCH_2MgCl}$ was used. Compound **4** is soluble in common organic solvents including hexane and highly air sensitive in both the solid state and solutions. In the ^{1}H NMR spectrum, the methyl protons of the trimethylsilylmethyl groups appear as a singlet at δ 0.31 ppm, indicating that the two alkyl groups are mutually cis and opposite the dtbpy ligand. The diastereotopic methylene protons appear as two doublets at δ 0.75 and 2.14 ppm (J = 11.4 Hz). We have not been able to obtain single crystals of **4** for structure determination. It may be noted that alkylation of $\mathrm{Ir(dtbpy)Cl_3(DMF)}$ with $\mathrm{Me_3SiCH_2MgCl}$ led to C−Si cleavage and formation of the silyl compound $\mathrm{Ir(dtbpy)(SiMe_3)(Me)(CH_2SiMe_3)}$.[18] Unsaturated **4** reacted with Lewis bases readily to give adducts. For example, treatment of

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(21) Frei, G.; Zilian, A.; Raeslli, A.; Gudel, H. U.; Burgi, H. B. *Inorg. Chem.* **1992**, *31*, 4766.

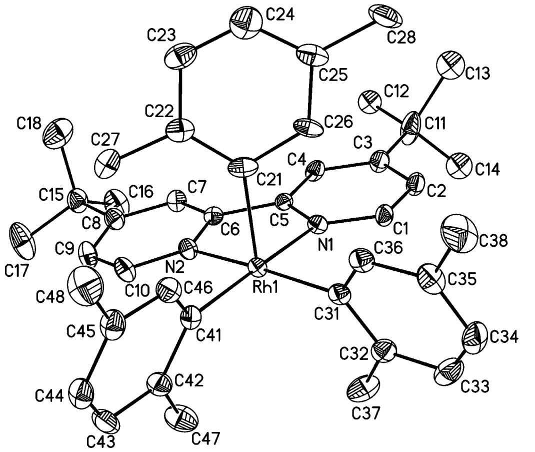


Figure 2. Molecular structure of Rh(dtbpy)(C_8H_9)$_3$ (**6**). The ellipsoids are drawn at 40% probability level.

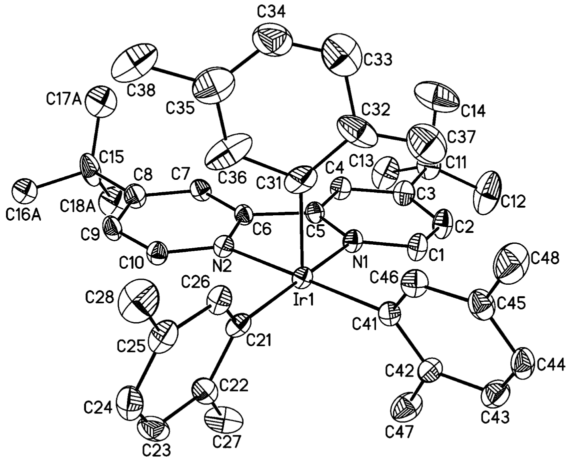


Figure 3. Molecular structure of Ir(dtbpy)(C_8H_9)$_3$ (**7**). The ellipsoids are drawn at 40% probability level.

4 with PPh_3 afforded an air-sensitive solid analyzed as Rh(dtbpy)(CH_2SiMe_3)$_2$Cl(PPh_3) (**5**).[22]

Rh and Ir Triaryl Compounds. Transmetalation of M(dtbpy)-Cl_3(DMF) with a variety of aryl Grignard reagents RMgX (R = phenyl, mesityl, 2-methylphenyl, etc.) has been attempted. However, in most cases, intractable brown materials were obtained. For the reaction with C_8H_9MgBr (C_8H_9 = 2,5-dimethylphenyl), we were able to isolate crystalline products that have been structurally characterized. Thus, treatment of M(dtbpy)Cl_3(DMF) with 3 equiv of C_8H_9MgBr afforded the triaryl compounds M(dtbpy)(C_8H_9)$_3$ (M = Rh (**6**), Ir (**7**)), isolated as air-stable orange and brown crystals, respectively (Scheme 2). Both compounds are soluble in common organic solvents including hexane. The ^{1}H NMR spectra of **6** and **7** show overlapping singlets at δ 1.77−2.18 and 2.15−2.40 ppm, respectively, due to the methyl protons of the aryl ligands.

The solid-state structures of **6** and **7** have been established by X-ray crystallography. Figures 2 and 3 show the molecular structures of **6** and **7**, respectively; selected bond lengths and angles are collected in Table 3. For each of the two compounds, the geometry around the metal center is pseudo-square-pyramidal with one aryl ligand occupying the apical position. No agostic interactions were found between the metal center and the aryl ligand despite the 16-electron configuration of the compounds. For **6**, the Ir is displaced by ca. 0.152 Å above the N_2C_2 plane. A similar displacement (0.165 Å) was found for **7**. The Rh−C distances for the aryl ligands in **6** are similar (2.014(3), 2.013(3), and 2.013(3) Å) and compare well with the Rh−C(aryl) distance in **2**. For **7**, the Ir−C distance for the apical aryl ligand (1.988(6) Å) is slightly shorter than those with equatorial ones (2.026(5) and 2.041(5) Å). The Rh−N and Ir−N distances are similar to those in **2** and **D**, respectively.

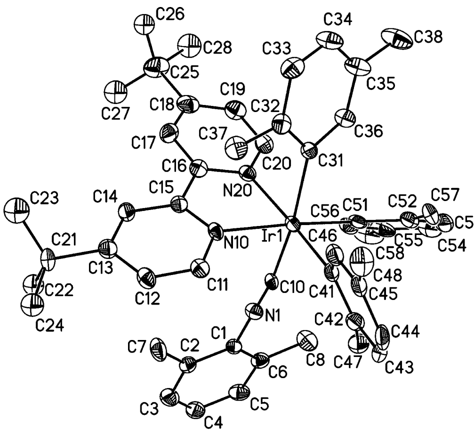
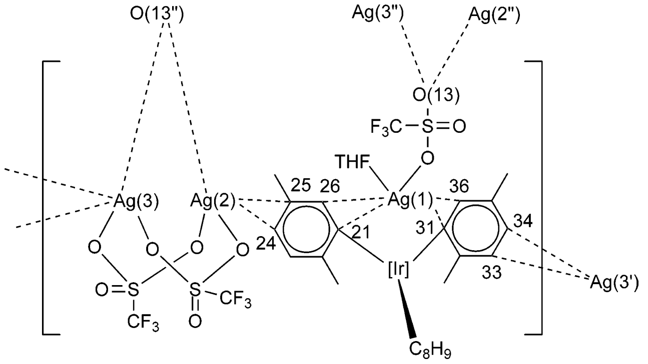


Figure 4. Molecular structure of Ir(dtbpy)(C_8H_9)$_3$(CNxyl) (**8**). The ellipsoids are drawn at 40% probability level.

Scheme 3



As expected, coordinately unsaturated **6** and **7** react with Lewis bases to give six-coordinated adducts. For example, treatment of **7** with CO afforded the CO adduct that exhibits an IR C−O band at 1980 cm^{-1}. No acyl C−O band was observed, indicating CO did not insert into the Ir−C bonds. We have not been able to crystallize this CO adduct for analysis. Treatment of **7** with 2,6-dimethylphenyl isocyanide (xylNC) gave crystalline Ir(dtbpy)(C_8H_9)$_3$(xylNC) (**8**), which has been characterized by X-ray crystallography. Figure 4 shows the molecular structure of **8**; selected bond lengths and angles are listed in Table 4. The geometry around Ir is pseudo-octahedral with the isocyanide ligand opposite the apical aryl group. The Ir−C(apical) distance of 2.151(5) Å is longer than that in **7** due to the trans effect of the isocyanide ligand, whereas the Ir−C(equatorial) distances (2.094(5) and 2.090(5) Å) are similar to those of the latter.

Reaction of 7 with Silver Triflate. The cyclic voltammogram of **7** in CH_2Cl_2 exhibits a reversible couple at 0.18 V vs $Cp_2Fe^{+/0}$, which is tentatively assigned as the Ir(IV/III) couple, whereas **6** is redox inactive in the range −2.0 to 1.0 V. A similar Ir(IV/III) potential has been found for **D** (0.02 V).[18] The Ir(IV/III) potential for **7** is less positive than those for related Ir(III) triaryl compounds such as Ir(mes)$_3$ (0.48 V)[10] and *fac*-Ir(ppy)$_3$

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[22] Satisfactory analytical data were obtained for **5**: Anal. Calcd for $C_{44}H_{61}ClN_2PRhSi_2$: C, 62.7; H, 7.3; N, 3.3. Found: C, 62.4; H, 7.3; N, 3.5. We have not been able to obtain a good NMR spectrum of **5** due to its poor solubility in organic solvents except dichloromethane and chloroform, in which it decomposed to an unknown species.

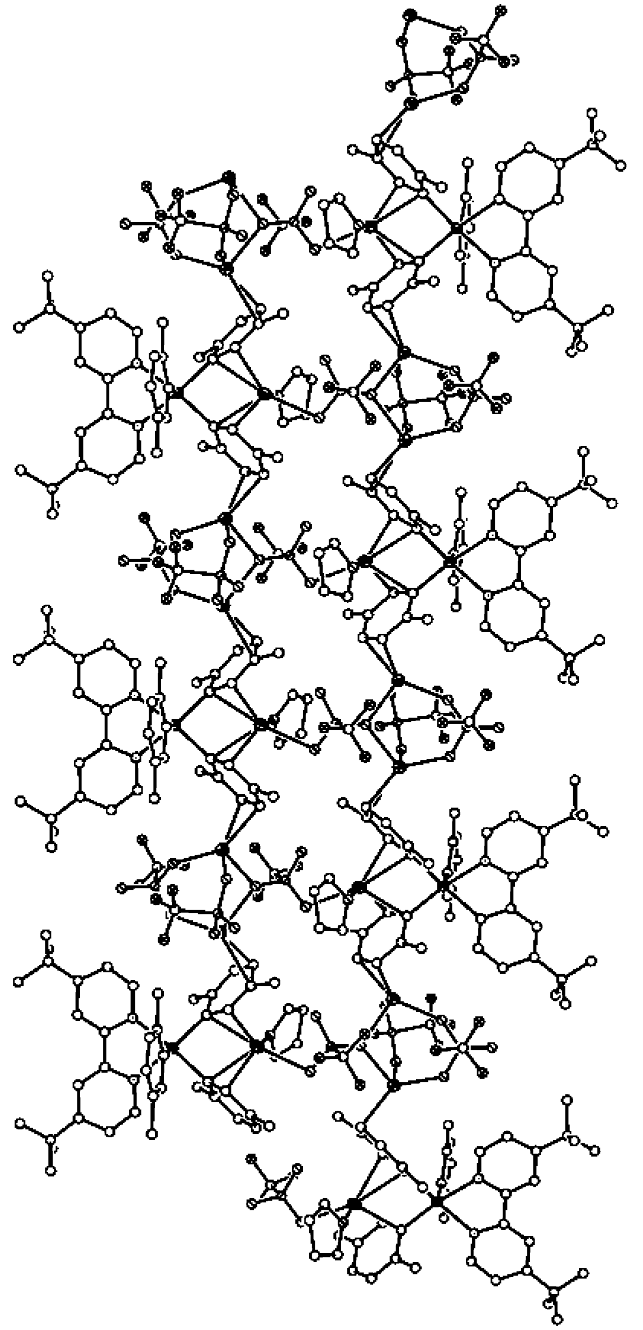

Figure 5. Double-chain structure of [Ir(dtbpy)$(C_8H_9)_3${Ag(OTf)(THF)}{$Ag_2(OTf)_2$}$]_\infty$ (**9**).

(0.31 V).[23] Despite the observation of a relatively low Ir(IV/III) potential, we have not been able to isolate the Ir(IV) aryl species by chemical oxidation of **7** with Ag(OTf) in CH_2Cl_2. Interestingly, treatment **7** with Ag(OTf) in THF led to isolation of brown crystals, identified as polymeric [Ir(dtbpy)$(C_8H_9)_3$-{Ag(OTf)(THF)}{Ag(OTf)}$_2]_\infty$ (**9**) by X-ray diffraction. The ^{1}H NMR spectrum of **9** in $CDCl_3$ displays broad resonances that are characteristic of polymeric compounds and distinctly different from those for **7**, indicating that the polymeric structure of **9** remained intact in solution. In the solid state, **9** has a "double-chain" structure (Figure 4), comprising the repeat unit "Ir(dtbpy)$(C_8H_9)_3${Ag(OTf)(THF)}{$Ag_2(OTf)_2$}" (Scheme 3). A view of the repeat unit is shown in Figure 5; selected bond

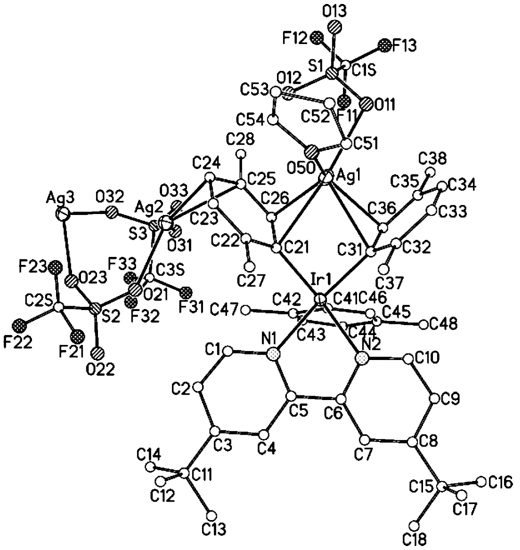

Figure 6. Structure of the repeat unit Ir(dtbpy)$(C_8H_9)_3${Ag(OTf)-(THF)}{$Ag_2(OTf)_2$} in **9** showing atom-labeling schemes of selected atoms. The prime and double-prime notations are used to indicate atoms in an adjacent repeat unit of the same chain and those in the adjacent chain, respectively.

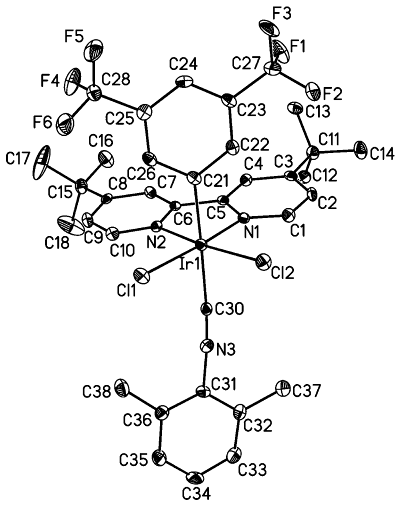

Figure 7. Molecular structure of Ir(dtbpy)(Ar_F)(CNxyl)$Cl_{1.4}Br_{0.6}$ (**11**). A disorder of the two halide sites was found. Only positions of the chlorides Cl(1) and Cl(2) are shown. The ellipsoids are drawn at 40% probability level.

lengths and angles are listed in Table 4. Although polymeric Ag(I) compounds containing polycyclic hydrocarbon ligands that bear two or more aromatic rings are well documented,[24] **9** is a rare example of such a coordination polymer derived from Ag(I) ions and transition metal-bound σ-aryl ligands. Similar to the parent compound **7**, the geometry around Ir in the repeat unit is pseudo-square-pyramidal with one aryl ligand occupying the apical position. The silver atom Ag(1) in the Ag(OTf)(THF) moiety binds to the two equatorial aryl ligands in an η^2-fashion (via C(21)−C(26) and C(31)−C(36), respectively). The Ag(1)−C distances ranging from 2.529(13) to 2.684(12) Å are typical for Ag(I) η^2-arene compounds.[24,25] The Ag−O(THF) and Ag−O(OTf) distances (2.3788(11) and 2.466(11) Å, respec-

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(23) Tamayo, A. B.; Alleyne, B. D.; Djurovich, P. I.; Lamansky, S.; Tsyba, I.; Ho, N. N.; Bau, R.; Thompson, M. E. *J. Am. Chem. Soc.* **2003**, *125*, 7377.

(24) See for examples: Munakata, M.; Wu, L. P.; Kuroda-Sowa, T.; Maekawa, M.; Suenaga, Y.; Sugimoto, K. *Inorg. Chem.* **1997**, *36*, 4903. (b) Zhong, J. C.; Munakata, M.; Kuroda-Sowa, T.; Maekawa, M.; Suenaga, Y.; Konaka, H. *Inorg. Chem.* **2001**, *40*, 3191.

(25) Lindeman, S. V.; Rathore, R.; Kochi, J. K. *Inorg. Chem.* **2000**, *39*, 5707.

tively) are normal. In the $Ag_2(OTf)_2$ moiety, the two triflate ligands bind to the two Ag atoms Ag(2) and Ag(3) in a μ-κ^1O:κ^1O' fashion. Ag(2) binds to a C−C double bond (C(24)−C(25)) in one equatorial aryl ligand, while Ag(3) binds to a C−C double bond (C(33′)−C(34′)) of another equatorial aryl ligand in the adjacent repeat unit (Scheme 3). The two polymer chains are linked together via interactions between the triflate oxygen O(13) and Ag(2″) and Ag(3″) of the adjacent polymer chain.

Ir(III) 3,5-Bis(trifluormethy)phenyl Complexes. To study the effect of electron-withdrawing substitutents on the structure and reactivity of σ-aryl compounds, Ir(III) compounds with a 3,5-bis(trifluoromethyl)phenyl (Ar_F) ligand have been synthesized. Alkylation of Ir(dtbpy)Cl_3(DMF) with 3 equiv of Ar_FMgBr led to isolation of the monoaryl compound [Ir(dtbpy)(Ar_F)(DMF)$Cl_{1.4}Br_{0.6}$] (**10**). The bromide in **10** was apparently derived from the Grignard reagent Ar_FMgBr. Although excess Grignard reagent was used, only the monoaryl complex was isolated. The ^{1}H NMR spectrum of **10** shows three sets of resonances due to the Ar_F ligand, indicating that the sample contained a mixture of three species. The positive-ion FAB mass spectrum shows the molecular ion peaks at *m*/*z* 744, 788, and 833, which are attributed to $[Ir(dtbpy)(Ar_F)Cl_2]^+$, $[Ir(dtbpy)(Ar_F)(Cl)(Br)]^+$, and $[Ir(dtbpy)(Ar_F)Br_2]^+$, respectively. Therefore, we believe that **10** is composed of three mixed halide compounds [Ir(dtbpy)(Ar_f)(DMF)Cl_2], [Ir(dtbpy)(Ar_F)(DMF)(Cl)(Br)], and [Ir(dtbpy)(Ar_F)(DMF)Br_2]. The presence of bromide in **10** has been further confirmed by an X-ray diffraction study of its isocyanide adduct (**11**) (vide infra).

Treatment of **10** with 2,6-dimethylphenyl isocyanide afforded the adduct [Ir(dtbpy)(Ar_F)(CNxyl)$Cl_{1.4}Br_{0.6}$] (**11**). Similar to **10**, the ^{1}H NMR spectrum of **11** displays three sets of resonances in the aromatic region due to the Ar_F group. The positive-ion FAB mass spectrum of **11** shows molecular ion peaks at *m*/*z* 884 and 840 corresponding to $[Ir(dtbpy)(Ar_F)(CNxyl)Br]^+$ and $[Ir(dtbpy)(Ar_F)(CNxyl)Cl]^+$, respectively. The structure of **11** has been established by an X-ray diffraction study. A view of the molecule is shown in Figure 7; selected bond lengths and angles are listed in Table 6. The crystal structure features an imposed disorder for the two halide sites with occupancies of 0.7 and 0.3 for Cl and Br, respectively. Similar to **8**, the geometry of **11** around Ir is pseudo-octahedral with the aryl group opposite the isocyanide. The Ir−C(Ar_F) distance in **11** (2.068(4) Å) is slightly shorter than the Ir−C(axial) in **8**, possibly due to the inductive effect of the electron-withdrawing CF_3 groups. The Ir−C(isocyanide) and Ir−N distances (2.001(5) and av 2.047(3) Å) compare well with those in **8**.

Conclusions

In summary, we found that alkylation of Rh(dtbpy)Cl_3(DMF) with $PhMe_2CCH_2MgCl$ resulted in the formation of rhodacyclic compound **2**, which features an agostic interaction between Rh and an ortho phenyl C−H group of the neophyl ligand. Compound **2** binds to CO to give an adduct without migratory insertion. We have synthesized dtbpy-supported Rh(III) and Ir(III) triaryl compounds that exhibit pseudo-square-pyramidal geometry in the solid state. No migratory insertion was found when **7** reacted with CO and isocyanide. Treatment of the Ir(III) triaryl with silver triflate in THF afforded an Ir/Ag double-chain polymer, in which the Ag(I) ions bind to C−C double bonds of the aryl ligands in an η^2-fashion.

Acknowledgment. We thank Dr. Herman H. Y. Sung for solving the crystal structures. The financial support from the Hong Kong Research Grants Council (project no. 601705) is gratefully acknowledged. Q.-F.Z. thanks the Science and Technological Fund of Anhui Province, P. R. China, for the Outstanding Youth Award (06046100).

Supporting Information Available: Tables of crystal data, final atomic coordinates, anisotropic thermal parameters, and complete bond lengths and angles for complexes **2**, **6**$\cdot 1/2C_7H_8$, **7**$\cdot 1/2C_6H_6$, **8**$\cdot 1/2C_6H_{14}\cdot C_4H_8O$, **9**$\cdot C_4H_8O$, and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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