

Unsymmetrically Bridging Aryls of Iridium

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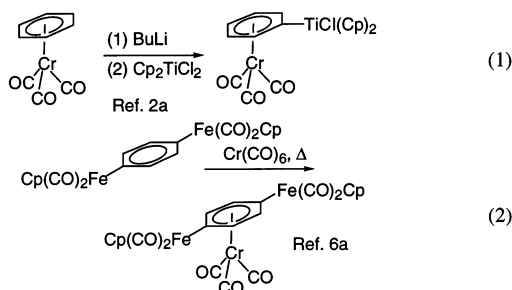
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The iridium(I) complex $[(\text{cod})\text{IrCl}]_2$ (**1**; cod = 1,5-cyclooctadiene) reacts with 2,6-disubstituted aryl Grignard reagents to give air-stable diiridium complexes $(\text{cod})\text{IrBr}(\mu, \kappa^1: \eta^6\text{-Ar})\text{Ir}(\text{cod})$ (Ar = 2,4,6-Me₃C₆H₂ (**2**), 2,6-Me₂C₆H₃ (**3**)). The aryl groups in these compounds are σ -bonded to one square-planar iridium(I) center and π -bonded to another (cyclooctadiene)-iridium(I) fragment. Spectroscopic and structural data indicate that the bonding is best described as a resonance hybrid between a zwitterionic σ -aryl/ η^6 -arene structure and a neutral carbene/ η^5 -cyclohexadienyl structure, with the former making a greater contribution. The resonance appears to stabilize both the iridium(I)–aryl σ - and π -bonds, with the result that the bridging aryl moiety is extremely chemically robust. The complexes react selectively at the square-planar iridium, undergoing ligand substitution of the cyclooctadiene or halide and oxidative addition of I₂.

Introduction

Both σ -bonded aryl groups and π -bonded η^6 -arenes have played pivotal roles in the history of organometallic chemistry. Indeed, these two classes of compounds have been intertwined since the beginning of this century, since Hein's "polyphenylchromium" species discovered in the early part of the 20th century proved to be η^6 -arene complexes formed via the intermediacy of σ -bonded aryls.¹ However, compounds in which an aryl group is simultaneously bonded both to one transition metal atom in a σ sense and to a second transition metal in a π sense generally require multistep procedures to prepare. The π -arene complex can be formed first, with the σ -bond being formed subsequently (e.g., eq 1). Methods for forming the metal–carbon σ -bond include lithiation followed by reaction with a transition metal halide,² directed metalation,³ and oxidative addition of a carbon–halogen⁴ or carbon–sulfur⁵ bond. Less commonly, the σ/π -bridging mode can be attained by initial formation of a σ -arylmatal complex followed by its π -complexation (e.g., eq 2).⁶



Here we describe the efficient preparation of diiridium complexes with σ/π -bridging 2,6-disubstituted aryl groups directly from an iridium halide and Grignard reagents.

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These compounds prove to be extraordinarily stable, with both the σ -linkage to the one iridium and the η^6 -linkage to the second iridium showing much greater chemical stability than is typically shown by unbridged aryl or arene complexes. A variety of ligand substitution and oxidation or reduction reactions can be carried out at the σ -bonded iridium center without disrupting the iridium–carbon σ -bond or the π -bonded iridium fragment. The unexpected stability of this diiridium fragment is rationalized on the basis of resonance stabilization by a carbene/ η^5 -cyclohexadienyl canonical form, which is supported by spectroscopic and structural studies.

Experimental Section

Unless otherwise noted, all procedures were carried out on the benchtop without special precautions to exclude air or

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moisture. When dry THF or Et₂O was required, it was vacuum transferred from sodium benzophenone ketyl. Benzene was dried over sodium. All other reagents were commercially available and used without further purification. ¹H and ¹³C-{¹H} NMR spectra were measured on a Varian-300 FT-NMR and are reported in parts per million downfield of TMS. Infrared spectra were recorded as evaporated films on KBr plates (unless otherwise noted) on a Perkin-Elmer Paragon 1000 FT-IR spectrometer. Elemental analyses were performed by M-H-W Laboratories (Phoenix, AZ).

Ir(cod)(Br)(μ-2,4,6-Me₃C₆H₂)Ir(cod) (2). In the drybox, a solution of [(cod)Ir(μ-Cl)]₂ (**1**; Strem, 300 mg, 0.447 mmol; cod = 1,5-cyclooctadiene) in dried THF (11 mL) in a 20 mL screw-cap vial was treated with 1 equiv of a 1.0 M THF solution of mesitylmagnesium bromide (Aldrich, 450 μL, 0.447 mmol). The vial was immediately capped and shaken rapidly, and the solution turned yellow. After standing for 1 h, the solution was opened to the air. The solution was transferred to a 50 mL round-bottom flask and diluted with fresh THF to a volume of 20 mL. Tetrabutylammonium bromide (Aldrich, 1.5 g, 4.65 mmol) was added and the mixture stirred for 22 h. The insoluble material was removed by suction filtration. After the solvent was removed in vacuo, the residue was slurried in methanol (50 mL) and the insoluble product was collected by suction filtration. The yellow crystals were washed with ether and air-dried to furnish 322.3 mg of analytically pure Ir(cod)(Br)(μ-2,4,6-Me₃C₆H₂)Ir(cod) (**2**, 90%). ¹H NMR (C₆D₆): δ 5.09 (m, 2H, alkene C-H trans to mes), 4.63 (s, 2H, Ar-H), 3.77 (m, 4H, (π-Ar)Ir(cod) alkene C-H), 2.48 (m, 2H, alkene C-H trans to Br), 2.34 (s, 6H, ortho-CH₃), 2.31 (m, 8H, cod CHH'), 1.83 (pseudo-q, *J* = 8 Hz, 4H, (η⁶-Ar)Ir(cod) CHH'), 1.78 (pseudo-t, *J* = 8 Hz, 2 H, (Ar)(Br)Ir(cod) CHH'), 1.55 (pseudo-t, *J* = 8 Hz, 2H, (Ar)(Br)Ir(cod) CHH'), 1.48 (s, 3H, para-CH₃). ¹³C-{¹H} NMR (CD₂Cl₂): δ 171.6 (*ipso* C), 112.6, 110.5, 95.9, 78.5, 62.6, 53.9, 33.8, 33.2, 30.6, 23.2, 18.7. IR (cm⁻¹): 2974 (s), 2946 (s), 2912 (s), 2872 (s), 2825 (s), 1441 (m), 1373 (m), 1324 (m) 1298 (w), 1262 (w), 1241 (w), 1207 (w), 1157 (w), 1076 (w), 1018 (m), 996 (m), 967 (w), 933 (w), 918 (w), 881 (w), 864 (w), 839 (w), 809 (w), 783 (w), 744 (m), 702 (w), 673 (w). Anal. Calcd for Ir₂C₂₅H₃₃Br: C, 37.54; H, 4.40. Found: C, 37.54; H, 4.59.

Ir(cod)(Br)(μ-2,6-Me₂C₆H₃)Ir(cod) (3). The 2,6-dimethylphenyl complex **3** was prepared as described above, substituting 2,6-dimethylphenylmagnesium bromide (Aldrich) for the mesitylmagnesium bromide. The yield was 310.3 mg (88%). ¹H NMR (C₆D₆): δ 5.17 (t, 6 Hz, 1H, *para*), 5.08 (m, 2H, alkene C-H trans to Ar), 4.57 (d, 6 Hz, 2H, *meta*), 3.84 (m, 4H, (π-Ar)Ir(cod) alkene C-H), 2.43 (m, 2H, alkene C-H trans to Br), 2.28 (s, 6H, CH₃), 2.25 (m, 8H, cod CHH'), 1.83 (pseudo-q, 8 Hz, 4H, (π-Ar)Ir(cod) CHH'), 1.77 (pseudo-t, 8 Hz, 2 H, (Ar)(Br)Ir(cod) CHH'), 1.53 (pseudo-t, 8 Hz, 2H, (Ar)(Br)Ir(cod) CHH'), 1.53 (pseudo-t, 8 Hz, 2H, (Ar)(Br)Ir(cod) CHH'). ¹³C-{¹H} NMR (CD₂Cl₂): δ 174.9 (*ipso* C), 113.4, 94.8, 93.4, 78.8, 61.6, 54.0, 33.7, 33.2, 30.5, 23.5. IR (cm⁻¹): 3060 (w), 3013 (w), 2971 (s), 2910 (s), 2871 (s), 2821 (s), 1472 (w), 1439 (m), 1401 (m), 1372 (s), 1324 (m), 1299 (w), 1263 (w), 1233 (w), 1206 (w), 1141 (w), 1015 (s), 993 (w), 967 (w), 910 (w), 839 (w), 820 (w), 807 (w). Anal. Calcd for Ir₂C₂₄H₃₃Br: C, 36.73; H, 4.24. Found: C, 36.64; H, 4.40.

Ir(cod)(I)(μ-2,6-Me₂C₆H₃)Ir(cod) (4). The iodo complex was prepared as described for the bromo complex **3** through the point where the crude reaction mixture was exposed to the air. At this point, the solution was diluted with acetone to a volume of 20 mL. Sodium iodide (Aldrich, 524.6 mg, 3.5 mmol, 7.8 equiv) was added and the mixture stirred 6 h in the dark. After filtration and evaporation of the solvent, the residue was slurried in methanol (50 mL) and the yellow crystalline product collected by suction filtration, washed with ether, and air-dried to furnish 316.2 mg of analytically pure iodo complex **4** (85%). ¹H NMR (CD₂Cl₂): δ 6.29 (t, 6 Hz, 1H, *para*), 5.59 (d, 6 Hz, 2H, *meta*), 4.40 (m, 2H, alkene C-H trans to Ar), 4.05 (m, 4H, (π-Ar)Ir(cod) alkene C-H), 2.32 (s, 6H, CH₃), 2.30 (m, 2H, alkene C-H trans to I), 2.26 (m, 4H, (Ar)-

(I)Ir(cod) CHH'), 2.11 (m, 4H, (π-Ar)Ir(cod) CHH'), 2.00 (pseudo-q, 8 Hz, 4H, (π-Ar)Ir(cod) CHH'), 1.64 (m, 2H, (Ar)-(I)Ir(cod) CHH'), 1.27 (m, 2H, (Ar)(I)Ir(cod) CHH'). IR (cm⁻¹): 2976 (s), 2908 (s), 2872 (s), 2822 (s), 1470 (w), 1438 (m), 1441 (m), 1371 (m), 1323 (m), 1298 (w), 1204 (w), 1152 (w), 1140 (w), 1014 (m), 966 (w), 908 (w), 836 (w). Anal. Calcd for Ir₂C₂₄H₃₃I: C, 34.64; H, 3.96. Found: C, 34.52; H, 4.06.

cis-Ir(CO)₂(Br)(μ-2,4,6-Me₃C₆H₂)Ir(cod) (5). Complex **2** (300 mg, 0.372 mmol) was dissolved in 10 mL of CH₂Cl₂. Carbon monoxide was bubbled for 10 min through the solution. The reaction mixture turned dark red within a few seconds, then faded to light yellow after 5 min. After the solvent was removed in vacuo, the residue was slurried in hexanes (50 mL) and the insoluble product was collected by suction filtration. The yellow crystals were washed with ether and air-dried to furnish 263.5 mg of **5** (94%). ¹H NMR (CD₂Cl₂): δ 5.88 (s, 2H, Ar-H), 3.97 (m, 4H, alkene C-H), 2.44 (s, 3H, *para*-CH₃), 2.38 (s, 6H, *ortho*-CH₃), 2.24 (m, 4H, cod CHH'), 2.06 (pseudo-q, 9 Hz, 4H, cod CHH'). ¹³C-{¹H} NMR (CD₂Cl₂): δ 184.6 (CO), 171.8 (CO), 146.0 (*ipso* C), 116.8, 113.5, 97.9, 63.2, 33.3, 24.6, 19.1. IR (cm⁻¹): 2943 (m), 2837 (m), 2040 (vs, ν_{CO}), 1957 (vs, ν_{CO}), 1443 (s), 1373 (s), 1328 (m), 1160 (m), 1020 (s), 954 (w), 915 (m), 875 (w), 841 (w), 711 (w), 676 (w), 608 (s), 562 (w), 495 (m). Anal. Calcd for Ir₂C₁₉H₂₃O₂Br: C, 30.52; H, 3.10. Found: C, 30.56; H, 2.99.

cis-Ir(CO)₂(Br)(μ-2,6-Me₂C₆H₃)Ir(cod) (6) was prepared analogously to **5**. The yield from 300 mg of **3** was 266 mg (95%). ¹H NMR (CD₂Cl₂): δ 6.57 (t, 6 Hz, 1H, *para*), 5.85 (d, 6 Hz, 2H, *meta*), 4.05 (m, 4H, alkene C-H), 2.35 (s, 6H, CH₃), 2.21 (m, 4H, cod CHH'), 2.01 (pseudo-q, 9 Hz, 4H, cod CHH'). ¹³C-{¹H} NMR (CD₂Cl₂): δ 184.5 (CO), 171.8 (CO), 148.3 (*ipso* C), 117.8, 97.0, 96.6, 62.2, 33.2, 24.8. IR (cm⁻¹): 2038 (vs, ν_{CO}), 1961 (vs, ν_{CO}), 1442 (s), 1411 (w), 1373 (s), 1326 (m), 1022 (m), 920 (w), 876 (w), 841 (w). Anal. Calcd for Ir₂C₁₈H₂₁O₂Br: C, 29.47; H, 2.88. Found: C, 29.38; H, 2.70.

cis-Ir(CO)₂(I)(μ-2,6-Me₂C₆H₃)Ir(cod) (7) was prepared analogously to **5**. The yield from 300 mg of **4** was 259.6 mg (92%). ¹H NMR (CD₂Cl₂): δ 6.55 (t, 6 Hz, 1H, *para*), 5.83 (d, 6 Hz, 2H, *meta*), 4.03 (m, 4H, alkene C-H), 2.27 (s, 6H, CH₃), 2.20 (m, 4H, cod CHH'), 2.02 (pseudo-q, 9 Hz, 4H, cod CHH'). IR (cm⁻¹): 2978 (m), 2940 (m), 2904 (m), 2037 (vs, ν_{CO}), 1951 (vs, ν_{CO}), 1476 (w), 1440 (s), 1400 (m), 1374 (m), 1329 (w), 1302 (w), 1264 (w), 1028 (m), 921 (w), 858 (w), 788 (w), 739 (w), 764 (w). Anal. Calcd for Ir₂C₁₈H₂₁O₂I: C, 27.68; H, 2.69. Found: C, 27.63; H, 2.46.

cis-Ir(CO)₂(2,6-Me₂C₆H₃)(μ-2,6-Me₂C₆H₃)Ir(cod) (8). *Cis*-Ir(CO)₂(I)(μ-2,6-Me₂C₆H₃)Ir(cod) (**7**, 200 mg, 0.256 mmol) was dissolved in 12 mL of dry THF in a 20 mL screw-cap vial in the drybox. The solution was treated with 5 equiv of a 1.0 M THF solution of 2,6-dimethylphenylmagnesium bromide (Aldrich, 1.28 mL, 1.28 mmol), and the vial was capped and allowed to stand at room temperature in the drybox for a week. The yellow crystals of **8** that deposited were collected by suction filtration in the air, washed with methanol followed by CH₂Cl₂, and air-dried to give 171.5 mg of **8** (88%). The compound was too insoluble to obtain ¹H or ¹³C NMR spectra. IR (Nujol mull, cm⁻¹): 2011 (vs, ν_{CO}), 1935 (vs, ν_{CO}), 1208 (w), 1156 (s), 1071 (w), 1005 (w), 972 (w), 892 (w), 768 (m). Anal. Calcd for Ir₂C₂₆H₃₀O₂: C, 41.13; H, 3.96. Found: C, 41.30; H, 4.01.

cis-Ir(CO)₂(2,4,6-Me₃C₆H₂)(μ-2,6-Me₂C₆H₃)Ir(cod) (9). The mixed diaryl complex **9** was prepared as described above, substituting mesitylmagnesium bromide for 2,6-dimethylphenylmagnesium bromide. The yield from 200 mg of **7** was 162.5 mg (82%). ¹H NMR (CD₂Cl₂): δ 6.62 (s, 2H, Me₃C₆H₂), 6.44 (t, 6.3 Hz, 1H, *para*, μ-2,6-Me₂C₆H₃), 5.76 (d, 5.7 Hz, 2H, *meta*, μ-2,6-Me₂C₆H₃), 4.06 (m, 4H, alkene C-H), 2.38 (s, 3H, *para*, Me₃C₆H₂), 2.34 (s, 6H, μ-2,6-(CH₃)₂C₆H₃), 2.23 (m, 4H, cod CHH'), 2.13 (s, 6H, *ortho*, Me₃C₆H₂), 2.03 (pseudo-q, 8.1 Hz, 4H, cod CHH'). IR (Nujol mull, cm⁻¹): 2010 (vs, ν_{CO}), 1934 (vs, ν_{CO}), 1208 (w), 1156 (m), 1078 (w), 1014 (w), 973 (m), 892

(w), 849 (m). Anal. Calcd for $\text{Ir}_2\text{C}_{27}\text{H}_{32}\text{O}_2$: C, 41.95; H, 4.14. Found: C, 41.77; H, 4.27. The compound was too insoluble to obtain ^{13}C NMR spectra.

***trans*- $\text{IrI}_3(\text{CO})_2(\mu\text{-}2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{Ir}(\text{cod})$ (10).** *cis*- $\text{Ir}(\text{CO})_2\text{-}(\text{I})(\mu\text{-}2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{Ir}(\text{cod})$ (7, 200 mg, 0.256 mmol) was dissolved in 7 mL of CH_2Cl_2 in a 20 mL screw-cap vial. To it was added iodine (65 mg, 0.256 mmol, 1.00 equiv) in 3 mL of CH_2Cl_2 . The vial was immediately capped and shaken rapidly; the solution turned light orange. The reaction mixture was layered with ether, and the orange crystals formed were filtered, washed with ether, and air-dried to furnish 185.4 mg of **10** (70%). ^1H NMR (CD_2Cl_2): δ 6.52 (t, 6 Hz, 1H, *para*), 5.92 (d, 6 Hz, 2H, *meta*), 4.11 (m, 4H, alkene C-H), 2.65 (s, 6H, CH_3), 2.31 (m, 4H, cod CHH'), 2.07 (pseudo-q, 9 Hz, 4H, cod CHH'). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 161.1 (CO), 114.6 (*ipso* C), 100.54, 100.47, 95.2, 65.9, 33.5, 30.95. IR (Nujol mull, cm^{-1}): 2053 (vs, ν_{CO}), 1158 (m), 992 (w), 917 (w), 838 (w). Anal. Calcd for $\text{Ir}_2\text{C}_{18}\text{H}_{21}\text{O}_2\text{I}_3$: C, 20.89; H, 2.03. Found: C, 21.00; H, 2.00.

$[\text{Ir}(\text{cod})(\text{mes})_2]\text{MgBr}_{0.5}\text{Cl}_{0.5}\cdot 6\text{THF}$ (11). In the drybox, the iridium(I) chloride dimer **1** (200 mg, 0.298 mmol), dry ether (10 mL), and dry benzene (2 mL) were placed in a 20 mL vial. The vial was securely capped and vigorously shaken to yield an orange solution of **1**. To the vial was added 5 equiv of 1.0 M mesitylmagnesium bromide in THF (1.5 mL, 1.49 mmol). The vial was immediately capped and shaken rapidly, and the solution turned dark red. Dark red needles of the diaryl anion **11** as a magnesium bromide salt were deposited overnight. The red needles of **11** that deposited were collected by suction filtration, washed with ether, and air-dried to give 476.5 mg of **11** (76%, assuming the composition of the counterion is that stated above). ^1H NMR (C_6D_6): δ 6.90 (s, 4H, Ar-H), 3.61 (br, 24H, THF), 3.44 (br, 4H, alkene C-H), 3.30 (br, 6H, *ortho*- CH_3), 2.48 (m, 4H, cod CHH'), 2.35 (s, 3H, *para*- CH_3), 1.92 (m, 4H, cod CHH'), 1.13 (br, 24H, THF).

X-ray Structure Determinations of $\text{Ir}(\text{cod})(\text{Br})(\mu\text{-}2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{Ir}(\text{cod})$ (2) and $\text{Ir}(\text{cod})(\text{Br})(\mu\text{-}2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{Ir}(\text{cod})$ (3). Yellow obelisks of the complex **2** were deposited after slow diffusion of ether into a solution of the complex in benzene. A $0.42 \times 0.18 \times 0.08$ mm crystal was glued to the tip of a glass fiber in the air and examined at 20°C on an Enraf-Nonius CAD4 diffractometer using Mo K α radiation with a graphite monochromator ($\lambda = 0.71037$ Å). The crystal was monoclinic, and its unit cell was determined based on 25 reflections with $13.1^\circ < \theta < 13.9^\circ$. A total of 8482 reflections in two octants (*hkl*, *h \bar{k} l*) with $2\theta < 50^\circ$ were collected. Crystal quality was monitored by recording three standard reflections approximately every 220 reflections measured; decay was 8%. An empirical absorption correction was applied ($\mu = 13.310$ cm^{-1} , transmission factors 0.242–0.770). After corrections for absorption and for Lorentz and polarization effects, 8171 unique reflections were obtained ($R_{\text{int}} = 0.0249$), of which one was suppressed during least-squares refinement due to highly negative apparent values of F_{obs} .

The space group was determined to be $P2_1/c$ based on systematic absences. The asymmetric unit contained two molecules of the complex. The four independent iridium atoms were located on a Patterson map, and remaining non-hydrogen atoms were found on difference Fourier syntheses. Hydrogens were placed in calculated positions. Final full-matrix least-squares refinement on F^2 converged at $R = 0.0516$ for 5391 reflections with $F_o > 2\sigma(F_o)$, $R = 0.1117$ for all data ($wR2 = 0.1187$, 0.1442, respectively.). All calculations used SHELXTL (Bruker Analytical X-ray Systems) with scattering factors and anomalous dispersion terms taken from the literature.⁷

Yellow blocks of the complex **3** were deposited after slow diffusion of ether into a solution of the complex in 1,2-dichloroethane. A $0.35 \times 0.32 \times 0.25$ mm crystal was glued to the tip of a glass fiber in the air and examined as described

above. The crystal was monoclinic (space group $P2_1/n$). The unit cell was determined based on 25 reflections with $15.07^\circ < \theta < 15.93^\circ$. A total of 4199 reflections with $2\theta < 50^\circ$ were collected. Crystal quality was monitored by recording three standard reflections approximately every 160 reflections measured; decay was negligible. An empirical absorption correction was applied ($\mu = 13.764$ cm^{-1} , transmission factors 0.4266–0.9678). The iridium atoms were located on a Patterson map, and remaining non-hydrogen atoms were found on difference Fourier syntheses and refined anisotropically. Hydrogens were placed in calculated positions. Final full-matrix least-squares refinement on F^2 converged at $R = 0.0415$ for 3262 reflections with $F_o > 2\sigma(F_o)$, $R = 0.0582$ for all data ($wR2 = 0.1076$, 0.1163, respectively.).

X-ray Structure Determinations of *cis*- $\text{Ir}(\text{CO})_2(\text{Br})(\mu\text{-}2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{Ir}(\text{cod})$ (5), *cis*- $\text{Ir}(\text{CO})_2(2,6\text{-Me}_2\text{C}_6\text{H}_3)(\mu\text{-}2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{Ir}(\text{cod})$ (8), and *trans*- $\text{Ir}(\text{CO})_2\text{I}_2\text{Br}(\mu\text{-}2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{Ir}(\text{cod})$ (12). Crystals of complex **5** were formed by slow diffusion of ether into a solution of the complex in 1,2-dichloroethane. A $0.5 \times 0.5 \times 0.3$ mm irregular fragment was coated with an inert oil and attached to the tip of a glass fiber in the cold N_2 stream of a Bruker Apex CCD diffractometer. An empirical absorption correction was applied using SADABS; decay was negligible. The crystals were orthorhombic, and the space group was determined to be $Pbca$ based on systematic absences. The iridium atoms were located on a Patterson map, and remaining non-hydrogen atoms were found on difference Fourier syntheses and refined anisotropically. Hydrogens were placed in calculated positions. Final full-matrix least-squares refinement on F^2 converged at $R = 0.0366$ for 4160 reflections with $F_o > 2\sigma(F_o)$, $R = 0.0421$ for all data ($wR2 = 0.0886$, 0.0905, respectively.).

Orange prisms of the diaryl complex **8** were deposited overnight directly from the reaction mixture. A $0.27 \times 0.28 \times 0.35$ mm crystal was mounted and examined as described above. The crystal was orthorhombic, and its space group was determined to be $Pbca$ based on systematic absences. The structure was solved and refined as described above. Final full-matrix least-squares refinement on F^2 converged at $R = 0.0232$ for 6330 reflections with $F_o > 2\sigma(F_o)$, $R = 0.0260$ for all data ($wR2 = 0.0617$, and 0.0630, respectively.).

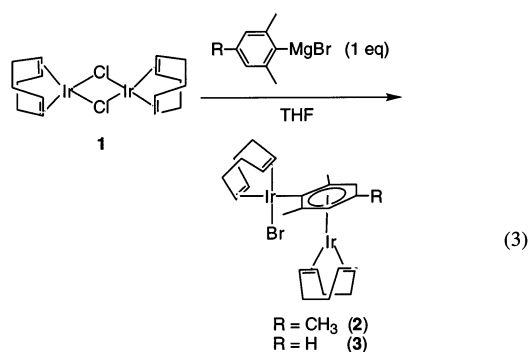
Complex **7** (25 mg, 0.032 mmol) was dissolved in 0.7 mL of CD_2Cl_2 in an NMR tube and treated with 1 equiv of iodine (8.1 mg, 0.032 mmol). The ^1H NMR spectrum of the reaction mixture showed a mixture of complexes similar to **10**, attributed to various isomers and halide compositions with an average composition of *trans*- $\text{Ir}(\text{CO})_2\text{I}_2\text{Br}(\mu\text{-}2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{Ir}(\text{cod})$ (**12**). Orange needles of **12** were deposited overnight. A $0.15 \times 0.08 \times 0.02$ mm crystal was mounted and examined as described above. The crystal was monoclinic, and its space group was determined to be $P2_1/n$ based on systematic absences. The structure was solved and refined as described above. The halide atoms were disordered and were modeled by refining the composition of each atom independently, subject to the global constraint of an overall 2:1 I:Br composition. Attempts to refine the atoms as iodine and bromine atoms in separate positions failed, and so each mixed-composition atom was given a single set of positional and thermal parameters. Final full-matrix least-squares refinement on F^2 converged at $R = 0.0376$ for 4197 reflections with $F_o > 2\sigma(F_o)$, $R = 0.0564$ for all data ($wR2 = 0.0873$, 0.1037, respectively.).

Results

Preparation and Characterization of Bridging Aryl Complexes. Treatment of the iridium chloride dimer $[(\text{cod})\text{IrCl}]_2$ (**1**; cod = 1,5-cyclooctadiene) with 1 mol of mesitylmagnesium bromide (mesityl = 2,4,6-trimethylphenyl) per mole of dimer results in the formation of the yellow, diamagnetic, air-stable complex

(7) *International Tables of Crystallography*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; Vol. C.

2. The ^1H NMR spectrum of **2** displays an unusual upfield shift of the aromatic protons of the mesityl group (δ 4.63 ppm in C_6D_6 ; upfield shifts are not as marked in nonaromatic solvents). This suggests that the aromatic ring is coordinated in a π fashion to an iridium atom. The NMR spectrum also shows two chemically inequivalent 1,5-cyclooctadiene ligands per mesityl group. One of these cyclooctadiene ligands is evidently bound in an unsymmetrical fashion (alkene protons at δ 5.09 and 2.48 ppm), while the other cyclooctadiene shows only a single set of alkene resonances in the ^1H NMR. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum shows 12 resonances, including a downfield resonance at 171.6 ppm assigned to the *ipso* carbon of the mesityl group. These data are consistent with a formulation of **2** as a diiridium complex containing one square-planar iridium(I) center σ -bonded to the mesityl group and a second iridium(I) center π -bonded to the same mesityl group (eq 3). The cyclooctadiene bound to the square-planar iridium shows inequivalent alkene resonances because of the distinct trans ligands, while the cyclooctadiene bound to the π -bonded iridium is fluxional. The fact that **2** contains a single halide can be inferred from the presence in the crude reaction mixture of a minor amount of a compound spectroscopically similar to **2**, assigned as its chloride analogue. The mixture is easily converted to pure bromo complex **2** upon treatment with tetrabutylammonium bromide. No signals attributable to a mixed chloride/bromide complex are observed.



An analogous bridging aryl complex **3** is formed from 2,6-dimethylphenylmagnesium bromide, with the aryl signals at δ 5.17 (*para*) and 4.57 (*meta*) again serving as a signature of the unusual σ,π -bridging mode. The $^3J_{\text{HH}}$ coupling constant between the *meta* and *para* hydrogens of 6 Hz is somewhat reduced from the usual 7–9 Hz coupling constant typically observed between *ortho* hydrogens in aromatics. This reduced coupling constant has been seen in other π -bonded areneiridium(I) complexes.⁸ Reactions with less hindered aryl Grignard reagents such as phenyl- or *o*-tolylmagnesium bromide do not produce analogous bridged compounds, judging from the absence of any resonances in the δ 4–5.5 ppm region of the ^1H NMR spectra of these reaction mixtures.

The structures of bromocyclooctadiene complexes **2** (Figure 1) and **3** (Figure 2) were determined by single-

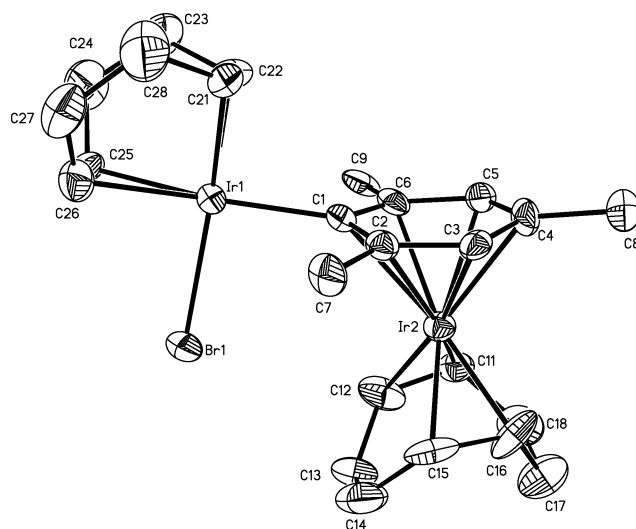


Figure 1. SHELXTL plot (30% thermal ellipsoids) of one of the two independent molecules of $\text{Ir}(\text{cod})(\text{Br})(\mu\text{-}2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{Ir}(\text{cod})$ (**2**).

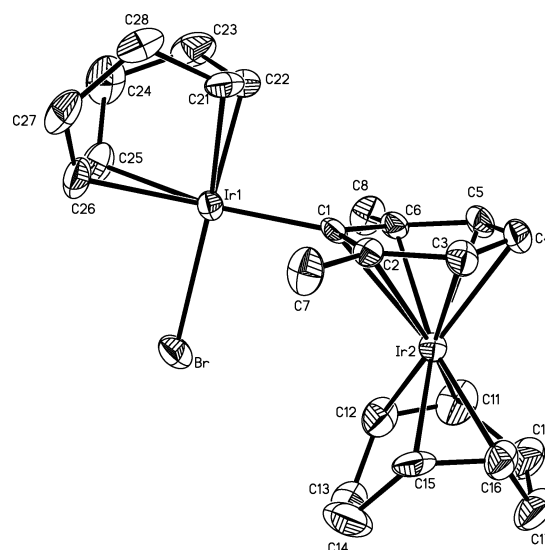


Figure 2. SHELXTL plot (30% thermal ellipsoids) of $\text{Ir}(\text{cod})(\text{Br})(\mu\text{-}2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{Ir}(\text{cod})$ (**3**).

crystal X-ray diffraction. Crystallographic details are listed in Table 1, and selected bond distances and angles in Table 2. The structures of both crystallographically independent molecules of **2** are very similar to each other and to the structure of **3**. The average Ir1-C1 bond length of 2.059(19) Å is significantly shorter than what is seen in the crystallographically characterized iridium(I) mesityl complexes $\text{Ir}(\text{mes})(\text{CO})(\text{dppe})$ (2.12 Å)^{9,10} and $\text{Ir}(\text{mes})(\text{CO})(\text{PPh}_3)_2$ (2.14 Å).¹¹ The π -bonded cyclooctadieneiridium(I) fragment is coordinated strongly to only five carbons, with the mean $\text{Ir2-C}(2\text{--}6) = 2.26\text{--}(4)$ Å (average over all three structures), while the mean Ir2-C1 bond distance is 2.42(3) Å. The *ipso* carbon atom is pulled significantly out of the plane formed by the other five carbon atoms, with C1 deviating from the C2–C3–C4–C5–C6 mean plane by 0.139 ± 0.026 Å. Distor-

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(8) (a) Grundy, S. L.; Smith, A. J.; Adams, H.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1984**, 1749–1754. (b) Torres, F.; Sola, E.; Martín; López, J. A.; Lahoz, F. J.; Oro, L. A. *J. Am. Chem. Soc.* **1999**, *121*, 10632–10633.

Table 1. Summary of Details of X-ray Crystallography

	Ir(cod)Br(μ -2,4,6-Me ₃ C ₆ H ₂)Ir(cod) (2)	Ir(cod)Br(μ -2,6-Me ₂ C ₆ H ₃)Ir(cod) (3)	Ir(CO) ₂ Br(μ -2,4,6-Me ₃ C ₆ H ₂)Ir(cod) (5)	Ir(CO) ₂ (2,6-Me ₂ C ₆ H ₃)(μ -2,6-Me ₂ C ₆ H ₃)Ir(cod) (8)	Ir(CO) ₂ BrI ₂ (μ -2,6-Me ₂ C ₆ H ₃)Ir(cod) (12)
empirical formula	C ₂₅ H ₃₅ BrIr ₂	C ₂₄ H ₃₃ BrIr ₂	C ₁₉ H ₂₃ BrIr ₂ O ₂	C ₂₆ H ₃₀ Ir ₂ O ₂	C ₁₈ H ₂₁ BrI ₂ Ir ₂ O ₂
fw	799.84	785.81	747.68	758.90	987.46
temperature (K)	293(2)	293(2)	173(2)	170(2)	170(2)
λ	0.71073 Å (Mo K α)	0.71073 Å (Mo K α)	0.71073 Å (Mo K α)	0.71073 Å (Mo K α)	0.71073 Å (Mo K α)
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>Pbca</i>	<i>Pbca</i>	<i>P</i> 2 ₁ / <i>n</i>
total data collected	8482	4199	32944	54340	23765
no. of indep reflns	8171	3902	4719	6802	5409
<i>a</i> (Å)	15.383(2)	7.815(2)	14.1633(11)	14.2533(6)	9.1441(3)
<i>b</i> (Å)	21.473(2)	20.328(3)	14.7640(11)	14.6197(6)	15.8388(6)
<i>c</i> (Å)	14.5907(10)	14.534(3)	18.7081(14)	21.3585(8)	15.0766(6)
α (deg)	90	90	90	90	90
β (deg)	102.942(8)	105.67(2)	90	90	92.5990(10)
γ (deg)	90	90	90	90	90
<i>V</i> (Å ³)	4697.1(9)	2223.2(7)	3912.0(5)	4450.7(3)	2181.32(14)
<i>Z</i>	8	4	8	8	4
calc ρ (g/cm ³)	2.262	2.348	2.539	2.265	3.007
cryst size (mm)	0.42 × 0.18 × 0.08	0.35 × 0.32 × 0.25	0.5 × 0.5 × 0.3	0.27 × 0.28 × 0.35	0.02 × 0.08 × 0.15
μ (mm ⁻¹)	13.031	13.764	15.644	11.968	16.860
<i>R</i> indices	<i>R</i> 1 = 0.0516,	<i>R</i> 1 = 0.0415,	<i>R</i> 1 = 0.0366,	<i>R</i> 1 = 0.0232,	<i>R</i> 1 = 0.0376,
[<i>I</i> > 2 σ (<i>I</i>)] ^a	w <i>R</i> 2 = 0.1187	w <i>R</i> 2 = 0.1076	w <i>R</i> 2 = 0.0886	w <i>R</i> 2 = 0.0617	w <i>R</i> 2 = 0.0873
<i>R</i> indices (all data) ^a	<i>R</i> 1 = 0.1117,	<i>R</i> 1 = 0.0582,	<i>R</i> 1 = 0.0421,	<i>R</i> 1 = 0.0260,	<i>R</i> 1 = 0.0564,
	w <i>R</i> 2 = 0.1442	w <i>R</i> 2 = 0.1163	w <i>R</i> 2 = 0.0905	w <i>R</i> 2 = 0.0630	w <i>R</i> 2 = 0.1037
GOF (all data)	1.039	1.052	1.117	1.083	1.084

$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|; wR2 = (\sum [w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2)^{1/2}.$$

Table 2. Selected Bond Distances (Å) and Angles (deg) for Crystallographically Characterized Compounds

	Ir(cod)Br(μ -2,4,6-Me ₃ C ₆ H ₂)Ir(cod) (2), molecule 1	Ir(cod)Br(μ -2,4,6-Me ₃ C ₆ H ₂)Ir(cod) (2), molecule 2	Ir(cod)Br(μ -2,6-Me ₂ C ₆ H ₃)Ir(cod) (3)	Ir(CO) ₂ Br(μ -2,4,6-Me ₃ C ₆ H ₂)Ir(cod) (5)	Ir(CO) ₂ (2,6-Me ₂ C ₆ H ₃)(μ -2,6-Me ₂ C ₆ H ₃)Ir(cod) (8)	Ir(CO) ₂ BrI ₂ (μ -2,6-Me ₂ C ₆ H ₃)Ir(cod) (12)
Ir1—C1	2.082(15)	2.047(13)	2.049(9)	2.088(6)	2.124(3)	2.114(9)
Ir1—C21	2.10(2)	2.09(2)	2.113(11)			
Ir1—C22	2.04(2)	2.12(2)	2.100(11)			
Ir1—C25	2.171(15)	2.17(2)	2.182(11)			
Ir1—C26	2.19(2)	2.16(2)	2.176(11)			
Ir1—Br	2.489(2)	2.481(2)	2.5000(12)	2.4909(8)		
Ir1—C31				1.849(7)	1.878(4)	1.919(11)
Ir1—C32				1.897(7)	1.856(4)	1.924(11)
Ir1—C51					2.142(4)	
Ir2—C1	2.39(2)	2.443(12)	2.441(10)	2.385(6)	2.411(3)	2.383(9)
Ir2—C2	2.320(15)	2.304(15)	2.290(9)	2.319(6)	2.247(3)	2.315(9)
Ir2—C3	2.232(14)	2.17(2)	2.200(10)	2.213(6)	2.276(4)	2.198(10)
Ir2—C4	2.30(2)	2.33(2)	2.280(6)	2.309(6)	2.292(4)	2.272(11)
Ir2—C5	2.25(2)	2.26(2)	2.256(6)	2.292(4)	2.210(4)	2.283(10)
Ir2—C6	2.25(2)	2.227(15)	2.244(6)	2.248(4)	2.306(3)	2.241(10)
Ir2—C11	2.11(2)	2.13(2)	2.122(11)	2.147(7)	2.131(4)	2.115(11)
Ir2—C12	2.17(2)	2.12(2)	2.117(12)	2.119(6)	2.123(4)	2.122(10)
Ir2—C15	2.14(2)	2.153(15)	2.125(12)	2.132(6)	2.132(4)	2.143(9)
Ir2—C16	2.11(2)	2.129(14)	2.148(12)	2.141(7)	2.126(4)	2.161(10)
C1—Ir1—C21	88.6(7)	87.5(6)	88.4(4)			
C1—Ir1—C22	90.1(7)	89.5(7)	88.5(4)			
C21—Ir1—C26	80.6(8)	82.9(7)	81.0(5)			
C22—Ir1—C26	94.1(9)	94.0(8)	95.6(5)			
C1—Ir1—Br	93.3(4)	93.3(4)	94.3(3)	85.2 (2)		
C25—Ir1—Br	89.5(5)	92.5(5)	92.1(4)			
C26—Ir1—Br	91.1(6)	88.9(6)	90.0(4)			
C1—Ir1—C31				92.2(3)	91.86(15)	95.5(4)
C1—Ir1—C32				175.7(3)	174.88(14)	95.6(4)
C1—Ir1—C51					90.55(13)	
C31—Ir1—C32				91.9(3)	93.3(2)	168.8(4)
C31—Ir1—Br				177.1(2)		
C32—Ir1—Br				90.6(2)		
C31—Ir1—C51					177.51(15)	
C32—Ir1—C51					84.33(14)	

tion from planarity is also shown by the “fold angle” between the planes C2—C1—C3 and the C2—C6 mean plane, which averages $9.9 \pm 1.5^\circ$ in the three structures. The cyclooctadiene ligand on Ir1 is bound somewhat unsymmetrically, with longer Ir—C distances trans to the aryl ligand (2.17 vs 2.10 Å) due to the structural trans influence of the aryl group.

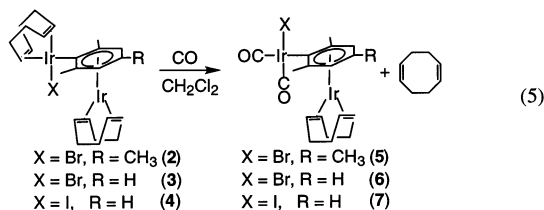
In the presence of excess mesitylmagnesium bromide, dimeric complexes such as **2** or **3** are not formed. Treatment of iridium chloride dimer **1** with excess mesitylmagnesium bromide (≥ 4 equiv per dimer) in Et₂O/benzene results in immediate formation of a red solution, from which red crystals of a dimesityl anion (**11**) as a salt with a THF-coordinated halomagnesium

cation are deposited overnight (eq 4). The NMR spectrum of **11** shows two equivalent mesityl groups for each cyclooctadiene ligand, which is symmetrical. Further confirmation of the connectivity of the anionic complex was given by a low-quality X-ray crystal structure, where extensive disorder of the cationic component and lattice solvent prevented satisfactory refinement. The isolated bridging aryl complex **2** does not react readily with added mesityl Grignard, with reactions taking several days and producing unidentified products, but no anion **11**. The isolated dimesityl anion **11** does not react with the iridium(I) chloride dimer **1** over several days at room temperature.



Ligand Substitution Reactions of Bridging Aryl Complexes. The bridging aryl complexes **2** and **3** undergo reaction selectively at the square-planar iridium center. For example, treatment of the bromo cyclooctadiene complex **3** with NaI results in the formation of the iodo cyclooctadiene complex **4**. This is analogous to the treatment of the crude reaction mixture of **2** and **3** with tetrabutylammonium bromide to convert any chloro complex to the bromo complex.

When carbon monoxide is bubbled through a solution of **2** in dichloromethane, the solution gives a transient dark red color that fades to pale yellow within a few seconds. The NMR spectrum of the final dicarbonyl complex **5** shows only one symmetrical set of cyclooctadiene resonances, suggesting that the cyclooctadiene bound to the square-planar iridium(I) center is completely displaced. This is confirmed by the detection of free cyclooctadiene by NMR in the crude reaction mixture (eq 5). The bromo- and iodocyclooctadiene complexes with bridging 2,6-dimethylphenyl groups (**3**, **4**) react similarly with carbon monoxide to form the corresponding bromo- and iododicarbonyl complexes **6** and **7**.



NMR and IR spectra of the products **5–7** indicate that the complexes have maintained the bridging aryl group but that the cyclooctadiene ligand of the square-planar iridium center has been replaced with a *cis*-dicarbonyl unit. This has been confirmed by an X-ray structure of the mesityl-bridged bromo dicarbonyl complex **5** (Figure 3). The Ir–CO bond distances of 1.849(7) and 1.897(7) Å are typical of iridium(I) carbonyl distances.^{9–12} The orientation of the square-planar iridium differs from what is seen in the dicyclooctadiene complexes **2** and **3**, in that CO, rather than bromide, is syn to the second iridium. Presumably this is due to a steric preference

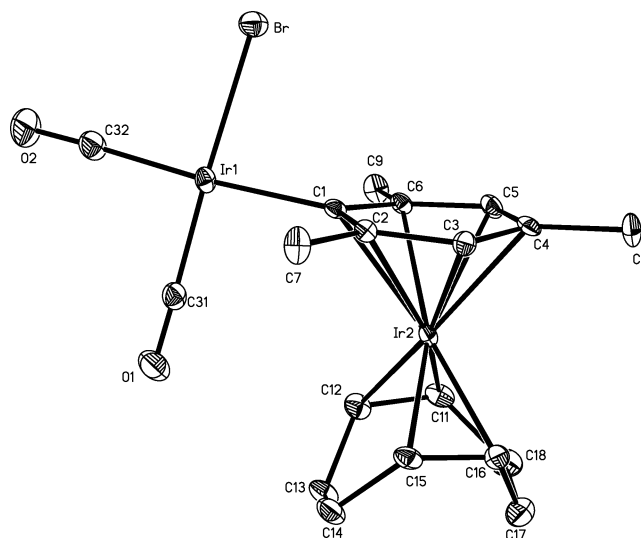
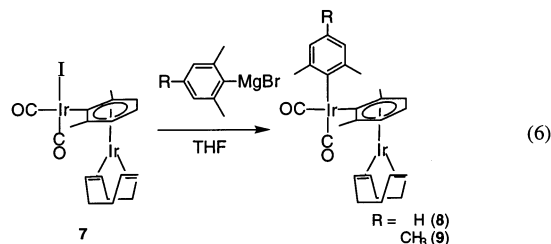


Figure 3. SHELXTL plot (30% thermal ellipsoids) of *cis*-Ir(CO)₂(Br)(μ-2,4,6-Me₃C₆H₂)Ir(cod) (**5**).

for the smaller ligand to approach the bulky (cyclooctadiene)iridium(I) fragment that is π -bonded to the arene. The Ir1–C1 bond distance of 2.088(6) Å is significantly longer, while the Ir2–C1 bond distance of 2.385(6) Å is significantly shorter, than the corresponding distances in the cyclooctadiene complexes **2** and **3**. The phenomenon of C1 being pulled out of the plane of the mesityl group is still apparent in **5**, but it is much less marked than in **2** and **3** (distance of Ir2 to C1 is 0.09 Å longer than the average distance of 2.28(4) Å to C2–C6, deviation of C1 from the mean plane = 0.071 Å, fold angle = 5.2°).

The bromo cyclooctadiene complex **2** undergoes no reaction with PPh₃ (60 °C, 3 days). It reacts very slowly at room temperature with 1 equiv of 1,2-bis(diphenylphosphino)ethane to give a mixture of products.

The iodo dicarbonyl complex **7** undergoes halide displacement over the course of several days at room temperature when treated with excess aryl Grignard reagents in THF (eq 6). Yellow air-stable crystals of aryl dicarbonyl complex **8** or **9** precipitate over the course of the reaction of **7** with 2,6-dimethylphenylmagnesium bromide or mesitylmagnesium bromide, respectively. The infrared spectra of the products display two terminal CO bands (e.g., 2011 and 1935 cm^{−1} for **8**). The shift of ~25 cm^{−1} to low frequency relative to the halo complexes **5–7** (e.g., 2038, 1961 cm^{−1} for **6**) is consistent with substitution of the more electron-donating aryl ligand for a halide. The iodo cyclooctadiene complex **4** reacts very slowly with aryl Grignard reagents to give a mixture of products.



The structure of the complex **8**, with both terminal and bridging 2,6-dimethylphenyl groups, was confirmed

(12) Schumann, H.; Cielusek, G.; Pickardt, J.; Bruncks, N. *J. Organomet. Chem.* **1979**, *172*, 359–365.

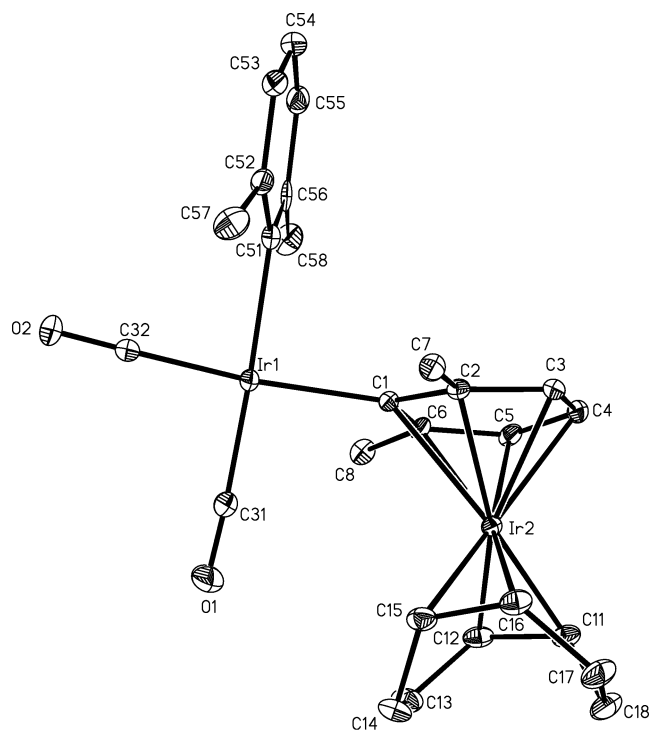
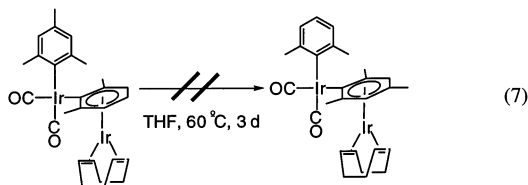


Figure 4. SHELXTL plot (30% thermal ellipsoids) of *cis*- $\text{Ir}(\text{CO})_2(2,6\text{-Me}_2\text{C}_6\text{H}_3)(\mu\text{-}2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{Ir}(\text{cod})$ (**8**).

by crystallography (Figure 4). The Ir1–C1 bond distance of the bridging aryl group (2.124(3) Å) is significantly shorter than the corresponding distance in the terminal aryl group (2.142(4) Å), although the difference is small. The distortions in the bridging aryl group (Ir2–C1 bond distance of 2.411(3) Å vs average distance from Ir2 to C2–C6 of 2.27(3) Å, deviation of C1 from the mean plane of 0.1129 Å, and fold angle of 8.1°) are all quite similar to those seen in the cyclooctadiene complexes **2** and **3** and show noticeably more distortion than is seen in the bromo dicarbonyl complex **5**.

Treatment of the 2,6-dimethylphenyl-bridged iodo dicarbonyl complex **6** with mesitylmagnesium bromide leads to a single isomer of the mixed aryl complex **9**. In the product the 2,6-dimethylphenyl group retains its bridging position (δ 5.76 for the *meta* protons in $\text{CD}_2\text{-Cl}_2$), and the incoming mesityl group is σ -bonded (δ 6.62 for the aromatic protons). The ^1H NMR spectrum of the mixed aryl complex **9** is unaffected by heating at 60 °C for 3 days, indicating that the π -bonded (cyclooctadiene)-Ir(I) fragment cannot flip between the 2,6-dimethylphenyl group and the mesityl group (eq 7).



Oxidation of Bridging Aryl Complexes. Oxidation of iridium aryls often induces reactivity at the iridium–carbon bond. For example, the iridium anion $[(\text{cod})\text{Ir}(\text{mes})_2]^-$ (**11**) reacts initially with iodine to form a green NMR-silent species that we presume to be the neutral iridium(II) complex $(\text{cod})\text{Ir}(\text{mes})_2$ analogous to other $\text{Ir}(\text{mes})_2\text{L}_2$ complexes prepared by Wilkinson

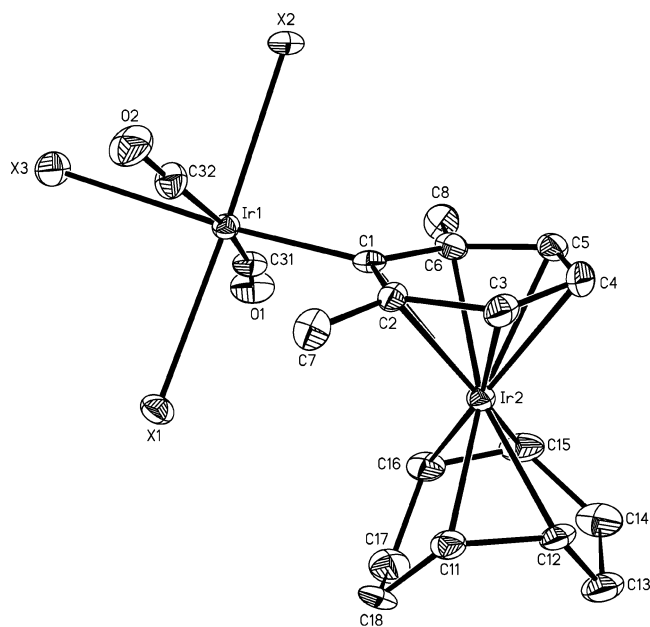


Figure 5. SHELXTL plot (30% thermal ellipsoids) of *trans*- $\text{Ir}(\text{CO})_2\text{I}_2\text{Br}(\mu\text{-}2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{Ir}(\text{cod})$ (**12**). The halide atoms X are disordered and were modeled by refining the composition of each atom independently, subject to the global constraint of an overall 2:1 I:Br composition.

(L = sulfides, phosphines).¹³ Further reaction with iodine results in iridium–carbon bond cleavage and formation of iodomesitylene.

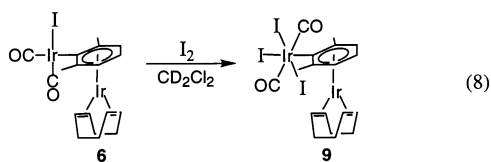
In contrast, the halo dicarbonyl complexes **6** and **7** undergo clean oxidative addition of molecular iodine at the square-planar iridium(I) center. For example, addition of 1 equiv of a dichloromethane solution of I_2 to a dichloromethane solution of iodo dicarbonyl complex **7** results in triiodo dicarbonyl complex **10** (eq 8). The infrared spectrum displays a single terminal CO band (at 2050 cm^{-1}), suggesting that the carbonyls have isomerized from *cis* to *trans* upon oxidation. The spectral features of the $(\text{cod})\text{Ir}(\text{I})$ fragment are largely unperturbed, indicating that this is a formally mixed-valence Ir(III)/Ir(I) complex.¹⁴ The bromo dicarbonyl complex **6** reacts with iodine in a similar fashion, forming a mixture of tri(halo) dicarbonyl compounds containing both bromides and iodides (**12**). A crystal from the latter reaction was analyzed by X-ray diffraction (Figure 5). The X-ray structure confirms that net oxidative addition of iodine to form an octahedral iridium(III) center with *trans* carbonyls ($\text{C31-Ir1-C32} = 168.8^\circ$) has taken place. The plane of the bridging aryl groups is staggered with respect to the four equatorial ligands on Ir1. Atom type disorder among the halides (refined as mixed atom types X) precludes obtaining accurate metrical data for the Ir–halogen bond lengths in this crystal.¹⁵ The Ir1–C1 bond distance of 2.114(9) Å is significantly longer than in the bromo dicarbonyl complex **5**. The average Ir–CO distance of 1.922 Å is substantially longer than the Ir(I)–CO distances in **5** (1.87 Å) and **8** (1.86 Å), as

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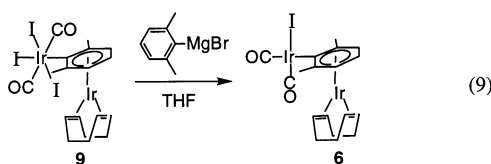
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expected due to decreased back-bonding in the Ir(III) complex. The deviation of C1 from the mean plane of the aryl group is 0.0901 Å, and the fold angle is 6.8°.

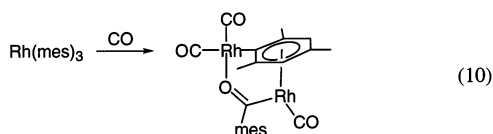


Rearrangement of carbonyls from cis to trans is rather unusual, as carbonyls generally prefer to occupy cis positions to minimize their competition for back-bonding. We see no sign of a cis isomer in the Ir(III) complex, but reduction to iridium(I), for example by reaction with 2,6-dimethylphenyl Grignard, restores the cis arrangement of the two CO groups (eq 9). In the presence of excess Grignard reagent, reduction to the iridium(I) iodo dicarbonyl complex **6** is immediate and is followed by much slower displacement of iodide to form the σ -bonded aryl complex **7** (eq 6).



Discussion

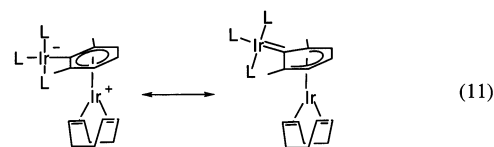
Structure, Reactivity, and Bonding in σ/π -Bridging Aryl Complexes. The chloro-bridged diiridium(I) complex [(cod)IrCl]₂ (**1**) reacts with 2,6-disubstituted aryl Grignard reagents to give air-stable diiridium complexes **2** and **3**. The aryl groups in these compounds show an unusual bridging mode, being σ -bonded to one square-planar iridium(I) center and π -bonded to another (cyclooctadiene)iridium(I) fragment. This bonding mode contrasts with the σ -bridged structures typical of main group elements such as Li,¹⁶ Al,¹⁷ and Mg,¹⁸ where the *ipso* carbons participate in relatively symmetrical three-center, two-electron bonds. The σ/π -bridged aryl most similar to the iridium complexes discussed here is the dirhodium complex (CO)₂Rh(μ,σ,η^6 -C₆H₂Me₃)(μ,η^1 (O), η^1 (C)-C₆H₂Me₃CO)Rh(CO), formed on carbonylation of Rh(mes)₃ (eq 10).¹⁹ Our observations indicate that this motif is readily accessible in iridium chemistry and that the stability of the bridging aryl group does not require the presence of an additional bridging ligand.



Indeed, the most noteworthy feature of the σ/π -bridging aryl groups is their remarkable chemical stability. All aryl-bridged diiridium complexes are stable

to air and moisture both as solids and in solution. Iridium(I) and rhodium(I) π -arene complexes are generally quite labile, often undergoing facile displacement even by weak ligands.²⁰ We have never observed displacement of the bridging aryl from the π -bonded (cod)-Ir^I fragment under any conditions. Ligand displacement of the cyclooctadiene of the σ -bonded iridium in **2** and **3** takes place rapidly with CO, but the bridging aryl is unaffected. Furthermore, the cyclooctadiene of the 18-electron (cod)Ir(η^6 -arene) fragment is not displaced under these conditions, which suggests that even a hapticity change of the π -bonded arene is not taking place. The dicarbonyl complex **5** is inert to triphenylphosphine, and even intramolecular arene exchange, as between the terminal and bridging aryls of (CO)₂Ir-(mes)(μ -2,6-Me₂C₆H₃)Ir(cod) (**9**) is not observed. Likewise, the σ -bond to the bridging aryl group appears to be more resistant to chemical attack than the σ -bond of typical hindered aryl ligands bonded to iridium. For example, iodine oxidation of the diaryl anion [(mes)₂-Ir(cod)]⁻ leads eventually to iodinolysis of the Ir-C bond, while aryl-to-carbonyl migration is induced by iodine oxidation of (dppe)Ir(mes)(CO).¹⁰ In contrast, the bridging aryl complex **7** reacts with iodine by simple oxidative addition, without any modification of the bridging 2,6-dimethylphenyl ligand.

The stability of the unsymmetrically bridging aryls can be rationalized based on considering the bonding in these species as a resonance hybrid of a zwitterionic σ -aryl/ η^6 -arene structure and a neutral carbene/ η^5 -cyclohexadienyl structure (eq 11). Such resonance stabilization would explain strengthening of both the σ and the π interactions relative to unbridged analogues.



Spectroscopic and structural data support this view of the bonding. The ¹³C NMR data for bromo cyclooctadiene complexes **2** and **3** are especially informative, showing downfield resonances for the *ipso* carbon at 171.6 and 174.9 ppm, respectively. The extreme low field of this resonance is highly suggestive of some degree of carbene character for the *ipso* carbon (δ 195–325 for iridium(I) carbene complexes).²¹ Structurally, distortion

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Table 3. Correlation between Electron Density at the Iridium Center σ -Bonded to the Aryl Group and Structural and Spectroscopic Properties of the Bridging Aryl Complexes

groups bonded to σ -bonded Ir in $L_n\text{Ir}(\mu\text{-Ar})\text{Ir}(\text{cod})$	most electron-rich \longrightarrow most electron-poor			
	Br(cod) (av 2a , 2b , 3)	(2,6-Me ₂ C ₆ H ₃)(CO) ₂ (8)	Br(CO) ₂ (5)	BrI ₂ (CO) ₂ (12)
Ir1–C1 (Å)	2.059(19)	2.124(3)	2.088(6)	2.114(9)
Ir2–C1 (Å)	2.425(30)	2.411(3)	2.385(6)	2.383(9)
deviation of C1 from mean plane (Å)	0.139	0.113	0.071	0.090
fold angle (deg)	9.9	8.1	5.2	6.8
ν_{CO} (cm ⁻¹)		2011, 1935	2040, 1957	2053 ^a
δ ¹³ C, C _{ipso} (ppm)	173.2	<i>b</i>	146.0	114.6 ^a

^a Measured for the triiodide complex **10**. ^b Not measured due to low solubility.

toward an η^5 structure is supported by the substantial elongation of the Ir2–C1 distance relative to the distance to the other five aromatic carbons (2.42 vs 2.26 Å in **2** and **3**) and by the fact that C1 is pulled significantly out of the plane formed by the other five carbon atoms (deviation of C1 from the mean plane is 0.139 ± 0.026 Å, and the “fold angle” between the planes C2–C1–C3 and the mean plane is $9.9^\circ \pm 1.5^\circ$ in the three structures). The relatively short σ -bonded Ir1–C1 distance of 2.06 Å is also consistent with some multiple bonding to this carbon.

This view of the bonding treats the σ -bonded iridium center as a π -donor to the *ipso* carbon of the bridging aryl. This is borne out by the structural similarity of the bridging aryl complexes to known iridium(I) complexes of arenes substituted with π -donors such as hydroxyl, as in [(cod)Ir(η^5 -HOC₆H₃-2,6-Ph₂)]⁺,²² or diphenylamino, in [Ir(TFB)(η^5 -PhNPh₂)]⁺ (TFB = tetrafluorobenzobarrelene).²³ The Ir2–C1 distance of 2.42 Å in **2** and **3** is close to that observed in the triphenylamine complex (2.457[11] Å), but about 0.1 Å shorter than that observed in the phenol complex (Ir–C_{ipso} = 2.53 Å). At least by this criterion, then, the (cod)BrIr^I fragment appears to be similar in its donor ability to Ph₂N, though somewhat weaker than OH. Structural distortions in (arene)Cr(CO)₃ complexes containing transition metals σ -bonded to the arene have been attributed to analogous π -donation from the σ -bonded metal center,²⁴ although inductive effects due to the electropositive metal substituent can also lead to distortions.²⁵ However, the chromium tricarbonyl complexes seem to show only moderate modification of their chemical properties due to σ -complexation of a second metal.²⁶ This contrast with the diiridium complexes described here may be due to the fact that in the chromium complexes it is the carbene/cyclohexadienyl resonance structure that is zwitterionic, thus decreasing its importance and making the complexes resemble the unperturbed σ -aryl/ η^6 -arene complexes. Little structural distortion toward a carbene/cyclohexadienyl structure was noted in anionic [η^6 -(CO)₅W]C₆H₅Cr(CO)₃[–] (where both canonical forms would contain one negative charge).²⁷

As the iridium center σ -bonded to the aryl group becomes more electron-deficient, the η^6 canonical form should become increasingly important relative to the η^5 /carbene form. This is generally supported by the structural and spectroscopic trends exhibited by the various compounds (Table 3). As the σ -bonded iridium fragments become increasingly electron-poor in the order (cod)BrIr^I < (CO)₂(2,6-Me₂C₆H₃)Ir^I < (CO)₂BrIr^I < (CO)₂X₃Ir^{III}, there is a general structural trend toward an η^6 structure (shortening of the Ir2–C1 distance, decreasing deviation of C1 from the mean plane) and away from any carbene contribution (lengthening σ -bonded Ir1–C1 distance and upfield shift in the ¹³C NMR of the *ipso* carbon). While the structural trends are not completely monotonic, they are generally consistent with this trend. The changes in the ¹³C NMR are particularly dramatic, with a >50 ppm upfield shift from the cyclooctadieneiridium(I) complexes **2** and **3** to the iridium(III) complex **10**, a trend opposed to the simple expectation that chemical shifts in the more electron-poor complex should shift downfield, not upfield.

An alternative way of formulating these bridging aryl complexes is to consider the aryl group with its π -bonded (cyclooctadiene)iridium(I) fragment as a neutral (formally zwitterionic) ligand bound to square-planar iridium(I) or octahedral iridium(III). When viewed in this way, the analogy of σ -Ar(Ir[cod]) to *N*-heterocyclic (Arduengo-type) carbenes is striking. Given the increasing importance of heterocyclic carbenes as supporting ligands in catalysis,²⁸ it is intriguing to consider the possibility of using neutral π -metalated/ σ -bonded aryl groups, with their potential for planar chirality, as ancillary ligands in catalytic systems.

Mechanism of Formation of Bridging Aryls. In contrast to the formation of bridging aryl complexes **2** and **3** on treatment of the iridium(I) dimer [(cod)Ir(μ -Cl)]₂ (**1**) with 1 mol of aryl Grignard per mole of dimer, reaction of excess mesitylmagnesium bromide leads to exclusive formation of the dimesityl anion [(cod)Ir(mes)₂][–] (**11**). Importantly, the isolated bridging mesityl cyclooctadiene complex **2** does *not* react readily with added mesityl Grignard, with reactions taking several days to give unidentified products which do not include anion **11**. Likewise, the isolated dimesityl anion **11** does not react with added iridium(I) chloride dimer **1** to form bridging aryl complex **2**. These observations indicate that neither the bridging aryl complex **2** nor the

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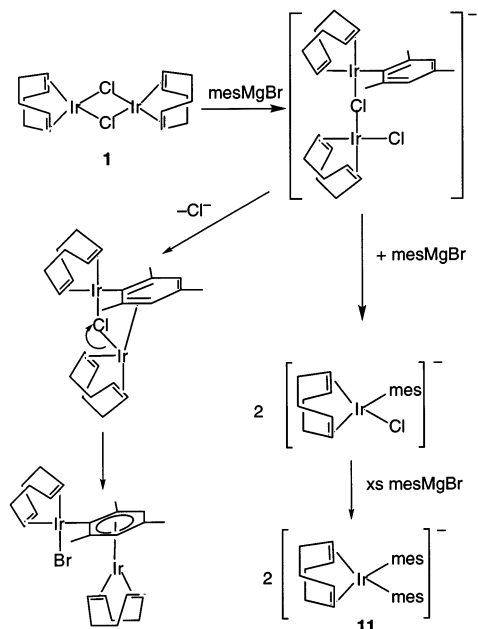
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Scheme 1. Proposed Mechanism of Reaction of Mesitylmagnesium Bromide with [(cod)Ir(μ -Cl)]₂ (1)



dimesityl anion **11** is an intermediate on the pathway leading to the other.

A plausible scenario to account for both of the mesityl products (Scheme 1) involves initial displacement of a chloride by mesityl Grignard to give an intermediate **13**. This intermediate has two possible fates. In the presence of excess Grignard, another chloride is displaced, leading to the formation of anion (**11**). In the absence of Grignard, unimolecular displacement of the second chloride by the σ -bonded mesityl group can take place, resulting in the formation of the bridging aryl complex **2**. While Scheme 1 depicts the crucial intermediate that precedes this branch point as having a bridging chloride ion and a nonbridging mesityl, other structures, such as one involving a σ -bridging mesityl group, are certainly possible. Indeed, while it is intuitively appealing that the dimeric structure of the starting material **1** is retained through the entire pathway to dimeric **2**, even that is by no means certain. The formation of the dirhodium complex (CO)₂Rh(μ , σ , η^6 -C₆H₂Me₃)(μ , η^1 (O), η^1 (C)-C₆H₂Me₃CO)Rh(CO) from monomeric Rh(mes)₃ (eq 10)¹⁹ indicates that monomeric intermediates may be reasonably invoked in the reaction. However, the fact that the reaction can cleanly give

either **2** or **11**, depending on the amount of added Grignard, strongly suggests the presence of a common intermediate in the two pathways. The notion that one branch of the mechanism involves a further attack by Grignard on a complex that already contains one aryl group provides a reasonable explanation for why less hindered aryl groups, such as phenyl or *o*-tolyl, lead only to anions and not bridging complexes. A monoaryl intermediate with the less hindered aryl groups should have more accessible iridium(I) sites and hence would undergo associative displacement more rapidly.

Conclusions

The iridium(I) chloride dimer (**1**) reacts with 2,6-disubstituted aryl Grignard reagents (1 mol per dimer) to yield air-stable diiridium complexes (**2** and **3**). The aryl groups in these complexes are σ -bonded to one iridium and π -bonded to a second. While this bridging mode isprecedented, this appears to be the first example where both σ and π complexation take place in a single chemical step. Spectroscopic and structural data indicate that the bonding is best described as a resonance hybrid between a zwitterionic σ -aryl/ η^6 -arene structure and a neutral carbene/ η^5 -cyclohexadienyl structure, and this resonance stabilization appears to contribute to the enhanced chemical stability of both the σ - and π -bonds relative to unbridged analogues. The complexes react selectively at the square-planar iridium without disturbing the π -bonded iridium center. In the presence of excess mesityl Grignard, the iridium(I) chloride dimer (**1**) reacts to form the monomeric diaryl-iridium(I) anion [(cod)Ir(mes)₂]⁻ (**11**), but this anion and the bridging aryl complexes cannot be readily interconverted.

Acknowledgment. We thank Dr. Maoyu Shang and Dr. Alicia Beatty for assistance with the X-ray crystal structures. Financial support from a DuPont Young Professor Award, from the Camille and Henry Dreyfus Foundation (New Professor Award), and from the Dow Chemical Company (Innovation Recognition Program) is gratefully acknowledged.

Supporting Information Available: Crystallographic data for **2**, **3**, **5**, **8**, and **12** in tabular form and in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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