Comparison of the Reactivity of M(allyl)$_3$ (M = Rh, Ir) with Donor Ligands

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Reactions of M(allyl)$_3$ [M = Rh, Ir] with a variety of donor ligands have been investigated. While both complexes are unreactive toward "hard" N- and O-donor ligands, "soft" ligands such as tolylisothiocyanate, tertiary phosphines, CO, and aryl isocyanides are readily added. Whereas ligand additions to Rh(allyl)$_3$ are often accompanied by reduction of the Rh(III) center, analogous reactions with Ir(allyl)$_3$ afford stable trivalent products containing σ-allyl ligands. The molecular structures of several derivatives are presented, including Ir(σ-allyl)-(π-allyl)$_2$(PPh$_3$), Ir(σ-allyl)$_2$(π-allyl)(PMe$_3$)$_2$, and Ir(σ-allyl)$_3$(C≡N-2,6-Me$_2$C$_6$H$_3$)$_3$.

Introduction

Investigations of the reactivity of metal allyl complexes have been central to the development of organometallic chemistry.[1] Despite the number of studies focused on compounds possessing group 9 metal−allyl fragments, little is known of the reactivity of the homoleptic tris(allyl) complexes of these metals.[2] In the case of cobalt, the scarcity of studies is likely due to its extreme air sensitivity and thermal instability of the parent (decomposes above −40 °C). One reaction of note is that with carbon monoxide, which gives Co(allyl)(CO)$_3$ and 1,5-hexadiene.[3] For iridium, the dearth of synthetic reports is most likely due to the low literature yield,[4] coupled with the high cost of starting materials. The only reaction reported is the protonolysis of Ir(allyl)$_3$ to form [Ir(allyl)$_2$(μ-Cl)]$_2$.[5] While reactions of tris(allyl)-rhodium with a variety of metal oxide supports have been reported,[6] the pioneering work by Powell and Shaw remains the key reference on solution reactions of Rh-(allyl)$_3$.[7] They showed that protonolysis of Rh(allyl)$_3$ gave [Rh(allyl)$_2$(μ-Cl)]$_2$, whereas addition of triphenylphosphine afforded monovalent Rh(allyl)(PPh$_3$)$_2$. We recently reported an improved preparation of Ir(allyl)$_3$ which has made reactivity studies of this complex practical.[8] In this contribution we compare and contrast the reactivity of tris(allyl)rhodium and -iridium with a variety of N, O, P, S, and C donor ligands.

Experimental Section

All manipulations were performed under inert atmosphere or vacuum using standard glovebox, vacuum-line, and Schlenk techniques. Solvents were dried by elution from columns of activated alumina and copper oxide BTS catalyst according to the procedure described by Grubbs et al.[9] All reactions were carried out at atmospheric pressure (600 mTorr at Los Alamos, elevation 7200 ft). *mer*-MCl$_3$(tht)$_3$ (M = Rh, Ir) were prepared by a modification of the literature procedure.[10] Allyllithium was prepared from tetraallyltin and *n*-buytllithium by a modification to the literature procedure.[11] All other chemicals were used as received. NMR spectra were recorded with a Varian UNITY series 300 MHz spectrometer, and all spectra were recorded at room temperature in C$_6$D$_6$ unless noted otherwise. All NMR solvents were stored over 4 Å molecular sieves. ^{31}P{^{1}H} chemical shifts are reported relative to an external 85% H$_3$PO$_4$ standard. Infrared spectra were measured with a Nicolet Magna 760 spectrometer at 4 cm^{-1} resolution as mineral oil mulls or solutions contained in an airtight sodium chloride cell. GC/MS analyses were performed on a HP 6980 GC system with a HP 5973 mass-selective detector.

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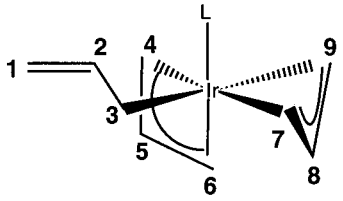
Elemental analyses were performed on a Perkin-Elmer 2400 system with a Series II CHNS/O analyzer and an AD-4 autobalance.



^{1}H NMR labeling scheme for **5**, **6** and **10**.

***mer*-IrCl$_3$(tht)$_3$ (1).** To a room-temperature suspension of IrCl$_3$·3H$_2$O (2.00 g, 5.67 mmol) in 2-methoxyethanol (100 mL) was added tetrahydrothiophene (2.50 mL, 28.4 mmol) with stirring. The solution was refluxed for 12 h, after which time water (150 mL) was added to the room-temperature solution. This treatment followed by filtration provided the crude product as a yellow powder. The product was further purified by recrystallization from boiling ethanol to yield **1** as yellow microcrystals in 91.5% yield (2.92 g, 5.19 mmol). ^{1}H NMR (CD_2Cl_2, 25 °C): δ 3.60 (m, 4H, SC*H*$_2$CH$_2$), 3.23 (m, 2H, SC*H*$_2$CH$_2$), 2.9 (overlapping m, 6H, SC*H*$_2$CH$_2$), 2.4−2.1 (overlapping m, 12H, SCH$_2$C*H*$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C): δ 36.92 (2C, S*C*H$_2$CH$_2$), 36.51 (4C, S*C*H$_2$CH$_2$), 30.49 (4C, SCH$_2$*C*H$_2$), 30.40 (2C, SCH$_2$*C*H$_2$). Anal. Calcd for $C_{12}H_{24}Cl_3S_3Ir$: C, 25.60; H, 4.30. Found: C, 25.70; H, 4.39.

***mer*-RhCl$_3$(tht)$_3$ (2).** RhCl$_3$(tht)$_3$ was prepared in the same manner as above from RhCl$_3$·3H$_2$O to provide orange microcrystals of **2** in 93.1% yield. ^{1}H NMR (CD_2Cl_2, 25 °C): δ 3.70 (m, 4H, SC*H*$_2$CH$_2$), 3.28 (m, 2H, SC*H*$_2$CH$_2$), 2.90 (overlapping m, 6H, SC*H*$_2$CH$_2$), 2.3−2.0 (overlapping m, 12H, SCH$_2$C*H*$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C): δ 37.69 (2C, S*C*H$_2$CH$_2$), 37.31 (4C, S*C*H$_2$CH$_2$), 30.38 (4C, SCH$_2$*C*H$_2$), 30.23 (2C, SCH$_2$*C*H$_2$). Anal. Calcd for $C_{12}H_{24}Cl_3S_3Rh$: C, 30.42; H, 5.11. Found: C, 30.43; H, 5.44.

Preparation of Ir(allyl)$_3$ (3). To a room-temperature suspension of IrCl$_3$(tht)$_3$ (0.509 g, 0.90 mmol) in Et$_2$O (40 mL) was added a solution of allyllithium (0.130 g, 2.70 mmol, in 10 mL of Et$_2$O) dropwise over 20 min with vigorous stirring. The reaction mixture was stirred for 14 h at room temperature, during which time the color of the solution changed from pale yellow to brown. The reaction mixture was then filtered and the residue rinsed with Et$_2$O (2 × 10 mL). The ether extract was reduced to dryness under vacuum, and the product was extracted with hexane (50 mL) and filtered. The hexane extract was reduced in volume to about 3 mL and transferred to a sublimator, where the remaining ether was removed and the brown residue was sublimed onto a coldfinger (−78 °C) at 10^{-5} Torr with mild heating (<60 °C). Sublimation afforded colorless microcrystalline Ir(allyl)$_3$ in 44.4% yield (0.126 g, 0.40 mmol). A solution of Ir(allyl)$_3$ can be prepared in over 80% yield (based on NMR analysis compared to an internal standard) from the reaction of IrCl$_3$(tht)$_3$ and allyllithium in benzene. However, the product can only be isolated in ca. 20% yield from sublimation (the poor yield is presumably due to "cosublimation" of Ir(allyl)$_3$ with the benzene). The solution prepared in this manner has been used to generate some of the complexes listed below with no effect on the product yields. ^{1}H NMR: δ 5.00 (m, 1 H, CH$_2$C*H*CH$_2$), 3.30 (m, 2 H, CH$_2$C*H*CH$_2$), 2.86 (d, 4 H, syn-C*H*$_2$CHC*H*$_2$), 2.75 (d, 2 H, syn-C*H*$_2$CHC*H*$_2$), 2.66 (d, 2 H, anti-C*H*$_2$CHC*H*$_2$), 1.72 (d, 4 H, anti-C*H*$_2$CHC*H*$_2$). ^{13}C{^{1}H} NMR: δ 91.98 (s, 1 C, CH$_2$*C*HCH$_2$), 82.17 (s, 2 C, CH$_2$*C*HCH$_2$), 38.07 (s, 2 C, *C*H$_2$CHCH$_2$), 28.33 (s, 4 C, *C*H$_2$CHCH$_2$). Anal. Calcd for $C_9H_{15}Ir$: C, 34.26; H, 4.79. Found: C, 34.57; H, 5.05.

Preparation of Rh(allyl)$_3$ (4). Bright yellow Rh(allyl)$_3$ was prepared in the same manner as above (in Et$_2$O) from RhCl$_3$(tht)$_3$ in 85.9% yield. ^{1}H NMR: δ 5.11 (m, 1 H, CH$_2$C*H*CH$_2$), 3.68 (m, 2 H, CH$_2$C*H*CH$_2$), 2.83 (d, 2 H, syn-C*H*$_2$CHC*H*$_2$), 2.65 (d, 4 H, syn-C*H*$_2$CHC*H*$_2$), 2.53 (d, 2 H, anti-C*H*$_2$CHC*H*$_2$), 1.53 (d, 4 H, anti-C*H*$_2$CHC*H*$_2$). ^{13}C{^{1}H} NMR: δ 100.18 (s, 1 C, $^1J_{RhC}$ = 4.3 Hz, CH$_2$*C*HCH$_2$), 95.06 (s, 2 C, $^1J_{RhC}$ = 4.0 Hz, CH$_2$*C*HCH$_2$), 48.23 (s, 2 C, $^1J_{RhC}$ = 9.2 Hz, *C*H$_2$CHCH$_2$), 41.22 (s, 4 C, $^1J_{RhC}$ = 9.1 Hz, *C*H$_2$CHCH$_2$). Anal. Calcd for $C_9H_{15}Rh$: C, 47.81; H, 6.69. Found: C, 47.76; H, 6.72.

Preparation of Ir(σ-allyl)(π-allyl)$_2$(SCN-Tol) (5). To a room-temperature solution of Ir(allyl)$_3$ (0.100 g, 0.32 mmol) in toluene (10 mL) was added tolylisothiocyanate (0.047 g, 0.32 mmol). The reaction mixture was stirred for 3 days at room temperature. The reaction solution was concentrated to ca. 2 mL and the product precipitated by addition of 10 mL of hexane to provide **5** as colorless crystals in 83.0% yield (0.122 g, 0.26 mmol). ^{1}H NMR: δ 6.77, 6.62 (d, 2 H, C$_6H_4$), 5.90 (m, 1 H, CH$_2$−C*H*=CH$_2$-**2**), 4.99 (overlapping ddt, 2 H, CH$_2$−CH=C*H*$_2$-**1**), 4.31 (ddt, 1 H, syn-C*H*$_2$CHC*H*$_2$-**6**), 3.93 (d d, 1 H, syn-C*H*$_2$CHC*H*$_2$-**9**), 3.82 (m, 1 H, CH$_2$C*H*CH$_2$-**5**), 3.65 (m, 1 H, CH$_2$C*H*CH$_2$-**8**), 3.34 (d, 1 H, anti-C*H*$_2$CHC*H*$_2$-**9**), 2.96 (ddt, 2 H, C*H*$_2$−CH=CH$_2$-**3**), 2.2 (overlapping d, 2 H, C*H*$_2$CHC*H*$_2$-**4**,**6**), 1.97 (s, 3 H, Me), 1.88 (d, 1 H, syn-C*H*$_2$CHC*H*$_2$-**7**), 1.50 (d, 1 H, anti-C*H*$_2$CHC*H*$_2$-**4**), 0.77 (d, 1 H, anti-C*H*$_2$CHC*H*$_2$-**7**). ^{13}C-{^{1}H} NMR: δ 132.74 (s, CH$_2$−*C*H=CH$_2$), 117.61 (s, CH$_2$−CH=*C*H$_2$), 81.37 (s, CH$_2$*C*HCH$_2$), 77.54 (s, CH$_2$*C*HCH$_2$), 45.85 (s, *C*H$_2$CHCH$_2$), 44.66 (s, *C*H$_2$CHCH$_2$), 39.60 (s, *C*H$_2$CHCH$_2$), 33.34 (s, *C*H$_2$CHCH$_2$), 28.34 (s, Me), 24.68 (s, *C*H$_2$−CH=CH$_2$).

Preparation of Ir(σ-allyl)(π-allyl)$_2$(PPh$_3$) (6). To a solution of Ir(allyl)$_3$ (0.100 g, 0.32 mmol) in 10 mL of toluene at 20 °C was added triphenylphosphine (0.083 g, 0.32 mmol). The reaction mixture was stirred for 2 h and then filtered. The filtrate was concentrated to ca. 2 mL and allowed to sit at 20 °C for 24 h to yield **6** as colorless crystals in 93% yield (0.170 g, 0.24 mmol). ^{1}H NMR: δ 7.43 (m, 5 H, Ph), 6.9 (m, 10 H, Ph), 6.39 (m, 1 H, CH$_2$−C*H*=CH$_2$-**2**), 4.61 (overlapping ddt, 2 H, CH$_2$−CH=C*H*$_2$-**1′**), 4.39 (m, 1 H, CH$_2$C*H*CH$_2$-**5**), 4.10 (m, 1 H, CH$_2$C*H*CH$_2$-**8**), 3.85 (ddt, $^3J_{HH}$ = 6.3 Hz, 1 H, syn-C*H*$_2$CHC*H*$_2$-**6**), 3.20 (d, $^3J_{HH}$ = 6.2 Hz, 1 H, syn-C*H*$_2$CHC*H*$_2$-**9**), 3.07 (m, 1 H, C*H*$_2$−CH=CH$_2$-**3**), 2.74 (br s, 1 H, syn-C*H*$_2$CHC*H*$_2$-**4**), 2.26 (d, $^3J_{HH}$ = 6.9 Hz, 1 H, syn-C*H*$_2$CHC*H*$_2$-**7**), 1.70 (d, $^3J_{HH}$ = 9.6 Hz, 1 H, anti-C*H*$_2$CHC*H*$_2$-**6**), 1.40 (dd, $^3J_{HH}$ = 10.6 Hz, $^3J_{HP}$ = 11.7 Hz, 1 H, anti-C*H*$_2$CHC*H*$_2$-**9**), 1.24 (ddt, 1 H, C*H*$_2$−CH=CH$_2$-**3**), 1.09 (dd, $^3J_{HH}$ = 9.2 Hz, $^3J_{HP}$ = 7.8 Hz, 1 H, anti-C*H*$_2$CHC*H*$_2$-**4**), 0.73 (dd, $^3J_{HH}$ = 11.0 Hz, $^3J_{HP}$ = 10.2 Hz, 1 H, anti-C*H*$_2$CHC*H*$_2$-**7**). ^{13}C{^{1}H} NMR: δ 151.58 (d, $^3J_{CP}$ = 2.3 Hz, CH$_2$−*C*H=CH$_2$), 134.69 (s, Aryl), 129.68 (s, Aryl), 128.17 (s, Aryl), 128.04 (s, Aryl), 102.60 (s, CH$_2$−CH=*C*H$_2$), 85.76 (s, CH$_2$*C*HCH$_2$), 78.94 (s, CH$_2$*C*HCH$_2$), 45.73 (d, $^2J_{CP}$ = 3.0 Hz, *C*H$_2$CHCH$_2$), 43.34 (d, $^2J_{CP}$ = 38.1 Hz, *C*H$_2$CHCH$_2$), 40.72 (s, *C*H$_2$CHCH$_2$), 32.46 (d, $^2J_{CP}$ = 2.5 Hz, *C*H$_2$CHCH$_2$), 11.22 (d, $^2J_{CP}$ = 3.7 Hz, *C*H$_2$−CH=CH$_2$). ^{31}P{^{1}H} NMR: δ 18.59 (s). IR (mineral oil): 1602 cm^{-1} (vw), ν(C=C). Anal. Calcd for $C_{27}H_{30}PIr$: C, 56.13; H, 5.23. Found: C, 55.93; H, 5.33.

Preparation of Ir(σ-allyl)$_2$(π-allyl)(Ph$_2$PC$_6$H$_4$PPh$_2$) (7). To a solution of Ir(allyl)$_3$ (0.100 g, 0.32 mmol) in 10 mL of toluene at 20 °C was added 1,2-bis(diphenylphosphino)benzene (0.142 g, 0.32 mmol). Addition of the phosphine resulted in an immediate color change to pale orange. The reaction mixture was heated briefly (10 min) to 85 °C to completely dissolve the phosphine and was then stirred for 14 h at room temperature. The orange solution was filtered and the filtrate concentrated to ca. 2 mL and allowed to sit at −35 °C for 24 h to yield **7** as colorless crystals in 89% yield (0.216 g, 0.28 mmol). ^{1}H NMR: δ 7.9−6.8 (24 H, Aryl), 6.35 (m, 1 H, CH$_2$−C*H*=CH$_2$-**A**), 5.09 (m, 1 H, CH$_2$−C*H*=CH$_2$-**B**), 4.96 (d, $^3J_{HH}$ = 9.9 Hz, 1 H, syn-CH$_2$−CH=CH$_2$-**B**), 4.88 (d, $^3J_{HH}$ = 16.8 Hz, 1 H, anti-CH$_2$−CH=CH$_2$-**B**), 4.8 (obscured m, 1 H, CH$_2$C*H*CH$_2$), 4.39 (d, $^3J_{HH}$ = 14.4 Hz, 1 H, anti-CH$_2$−CH=CH$_2$-**A**), 4.17 (d, $^3J_{HH}$ = 9.6 Hz, 1 H, syn-CH$_2$−CH=CH$_2$-**A**), 2.85 (br s, 1 H, syn-C*H*$_2$CHC*H*$_2$), 2.73 (d, 1 H, anti-C*H*$_2$CHC*H*$_2$), 2.69 (d, 1 H, anti-C*H*$_2$CHC*H*$_2$), 2.57 (m, 1 H, syn-C*H*$_2$CHC*H*$_2$), 2.0 (overlapping ddt, 3 H, C*H*$_2$−CH=CH$_2$), 1.72 (ddt, 1 H, C*H*$_2$−CH=CH$_2$). ^{13}C{^{1}H} NMR: δ 149.56 (s, CH$_2$−*C*H=CH$_2$), 148.06 (d, $^3J_{CP}$ =

6.0 Hz, $CH_2-CH{=}CH_2$), 144.9−127.8 (aromatic),106.46 (d, J_{CP} = 7.3 Hz, $CH_2-CH{=}CH_2$), 100.83 (s, $CH_2-CH{=}CH_2$), 97.39 (s, CH_2CHCH_2), 48.89 (s, CH_2CHCH_2), 48.75 (s, $^2J_{CP}$ = 39.4 Hz, CH_2CHCH_2), 18.95 (s, $^2J_{CP}$ = 79.5; 5.0 Hz, $CH_2-CH{=}CH_2$), 6.99 (s, $CH_2-CH{=}CH_2$). $^{31}P\{^1H\}$ NMR: δ 26.97, 23.65. IR (mineral oil): 1604 cm^{-1} (vw), ν(C=C). Anal. Calcd for $C_{39}H_{39}P_2Ir$: C, 61.48; H, 5.16. Found: C, 61.39; H, 5.37.

Preparation of Ir(σ-allyl)$_3$(Ph$_2$P(CH$_2$)$_2$P(Ph)(CH$_2$)$_2$PPh$_2$) (8). To a solution of Ir(allyl)$_3$ (0.100 g, 0.32 mmol) in 10 mL of toluene at 20 °C was added bis(2-diphenylphosphinoethyl)-phenylphosphine (0.169, 0.32 mmol). The reaction mixture was heated briefly (10 min) to 85 °C to completely dissolve the phosphine and was then stirred for 14 h at room temperature. The solution was filtered, and the pale yellow filtrate was concentrated to ca. 2 mL and allowed to sit at −35 °C for 24 h to yield **8** as colorless crystals in 91.8% yield (0.247 g, 0.29 mmol). ^1H NMR: δ 7.6−6.6(25 H, Ph), 6.9 (obscured m, 1 H, $CH_2-CH{=}CH_2$), 5.92 (m, 2 H, $CH_2-CH{=}CH_2$), 5.40 (ddt, 1 H, anti-$CH_2-CH{=}CH_2$), 5.04 (ddt, 1 H, syn-$CH_2-CH{=}CH_2$), 4.4 (overlapping ddt, 4 H, $CH_2-CH{=}CH_2$), 3.62 (m, 2 H, $CH_2-CH{=}CH_2$), 2.2 (obscured m, 4 H, $CH_2-CH{=}CH_2$). $^{13}C\{^1H\}$ NMR: δ 150.00 (s, 1 C, $CH_2-CH{=}CH_2$), 149.05 (s, 2 C, $CH_2-CH{=}CH_2$), 132.2−125.6 (aromatic), 106.73 (s, 1 C, $CH_2-CH{=}CH_2$), 105.82 (s, 2 C, $CH_2-CH{=}CH_2$), 29.9 (m, 4 C, $-CH_2-$), 13.29 (m, $^2J_{CP}$ = 78.7; 4.1 Hz, 2 C, $CH_2-CH{=}CH_2$), 12.77 (m, $^2J_{CP}$ = 79.6 Hz, 1 C, $CH_2-CH{=}CH_2$). $^{31}P\{^1H\}$ NMR: δ 34.87-(1P), −2.70 (2P). IR (mineral oil): 1608 cm^{-1} (vw), ν(C=C). Anal. Calcd for $C_{43}H_{48}P_3Ir$: C, 60.76; H, 5.69. Found: C, 60.71; H, 5.97.

Preparation of Ir(σ-allyl)$_2$(π-allyl)(PMe$_3$)$_2$ (9a). To a room-temperature solution of Ir(allyl)$_3$ (0.100 g, 0.32 mmol) in 10 mL of toluene was added trimethylphosphine (65 μL, 0.63 mmol). The reaction mixture was stirred for 14 h and then filtered. The filtrate was concentrated to ca. 2 mL and allowed to sit at −35 °C for 24 h to yield **9a** as colorless crystals in 96.5% yield (0.143 g, 0.31 mmol). Extended vacuum workup of the reaction mixture resulted in formation of a 50/50 mixture of **9a** and Ir(σ-allyl)(π-allyl)$_2$PMe$_3$ (**10**). Formation of the latter complex appears to be reversible, as addition of PMe_3 results in clean conversion of **10** back to **9a**. ^1H NMR: δ 5.8 (overlapping m, 2 H, $CH_2-CH{=}CH_2$), 4.82 (ddt, 1 H, syn-$CH_2-CH{=}CH_2$-**A**), 4.7 (overlapping ddt, 2 H, $CH_2-CH{=}CH_2$-**B**), 4.64 (ddt, 1 H, anti-$CH_2-CH{=}CH_2$-**A**), 3.83 (m, 1 H, CH_2CHCH_2), 2.96 (ddt, 2 H, anti-CH_2CHCH_2), 2.16 (d d, 2 H, syn-CH_2CHCH_2), 1.62 (m, 2 H, $CH_2-CH{=}CH_2$-**A**), 1.23 (d, 18 H, $^2J_{HP}$ = 8.7 Hz, PMe_3), 1.20 (m, 2 H, $CH_2-CH{=}CH_2$-**B**). $^{13}C\{^1H\}$ NMR: δ 148.56 (s, $^3J_{CP}$ = 3.2 Hz, $CH_2-CH{=}CH_2$), 147.13 (s, $^3J_{CP}$ = 3.6 Hz, $CH_2-CH{=}CH_2$), 109.52 (s, CH_2CHCH_2), 104.27 (s, $CH_2-CH{=}CH_2$), 104.06 (s, $CH_2-CH{=}CH_2$), 46.39 (d, $^2J_{CP-trans}$ = 32.4 Hz, CH_2CHCH_2), 46.35 (d, $^2J_{CP-trans}$ = 32.8 Hz, CH_2CHCH_2), 16.68 (s, $^1J_{CP}$ = 32.0 Hz, PMe_3), 0.43 (s, $^2J_{CP}$ = 4.6 Hz, $CH_2-CH{=}CH_2$), −2.66 (s, $^2J_{CP}$ = 5.4 Hz, $CH_2-CH{=}CH_2$). $^{31}P\{^1H\}$ NMR: δ −50.75.

Selected NMR data for **10**: ^1H, 6.42 (m, 1 H, $CH_2-CH{=}CH_2$-**2**), 4.80 (ddt, 1 H, anti-$CH_2-CH{=}CH_2$-**1**), 4.80 (ddt, 1 H, syn-$CH_2-CH{=}CH_2$-**1**), 4.1 (overlapping m, 2 H, CH_2CHCH_2-**5**,**8**), 3.21 (overlapping ddt, 2 H, syn-$CH2CHCH_2$-**6**,**9**), 2.74 (m, 1 H, $CH_2-CH{=}CH_2$-**3**), 2.60 (m, 1 H, syn-CH_2CHCH_2-**4**), 1.85 (overlapping m, 2 H, CH_2CHCH_2-**7**,**6**), 1.54 (d, 1 H, anti-CH_2CHCH_2-**9**), 0.94 (d, 9 H, $^2J_{HP}$ = 9.3 Hz, PMe_3), 0.78 (overlapping d, 2 H, anti-CH_2CHCH_2-**4**,**7**), 0.60 (t, 1 H, $CH_2-CH{=}CH_2$-**3**). $^{31}P\{^1H\}$ NMR: δ −44.53.

Preparation of Ir(σ-allyl)$_2$(π-allyl)[P(OPh)$_3$]$_2$ (9b). To a room-temperature solution of Ir(allyl)$_3$ (0.060 g, 0.19 mmol) in 5 mL of toluene was added triphenyl phosphite (0.118 g, 0.38 mmol). The reaction mixture was stirred for 24 h and then filtered. The filtrate was concentrated to ca. 1 mL, and the product was precipitated by addition of hexane (5 mL). The product was isolated by filtration to provide a colorless powder in 87.5% yield (0.155 g, 0.166 mmol). ^1H NMR: δ 7.2−6.7 (30 H, Ph), 6.31 (m, 1H, $CH_2-CH{=}CH_2$-**A**), 6.14 (m, 1H, $CH_2-CH{=}CH_2$-**B**), 4.87 (ddt, 1 H, syn-$CH_2-CH{=}CH_2$-**B**), 4.65 (overlapping ddt, 3 H, $CH_2-CH{=}CH_2$), 3.61 (m, 1 H, CH_2-CHCH_2), 3.06 (ddt, 2 H, anti-CH_2CHCH_2), 2.64 (d d, 2 H, syn-CH_2CHCH_2), 2.2 (overlapping m, 4 H, $CH_2-CH{=}CH_2$). $^{13}C-\{^1H\}$ NMR: δ 153.06 (m, $^3J_{CP}$ = 6.7 Hz, $CH_2-CH{=}CH_2$), 147.91 (m, $CH_2-CH{=}CH_2$), 113.68 (s, CH_2CHCH_2), 106.03 (s, $CH_2-CH{=}CH_2$), 104.86 (s, $CH_2-CH{=}CH_2$), 48.93 (m, $^2J_{CP-trans}$ = 47.5 Hz, $^2J_{CP-cis}$ = 9.8 Hz CH_2CHCH_2), 1.87 (br s, $CH_2-CH{=}CH_2$), −0.42 (m, $CH_2-CH{=}CH_2$). $^{31}P\{^1H\}$ NMR: δ 70.61. Anal. Calcd for $C_{45}H_{45}P_2O_6Ir$: C, 57.74; H, 4.85. Found: C, 57.86; H, 4.82.

Preparation of Rh(σ-allyl)$_2$(π-allyl)(PMe$_3$)$_2$ (9c). To a room-temperature solution of Rh(allyl)$_3$ (0.080 g, 0.35 mmol) in 10 mL of toluene was added trimethylphosphine (72 mL, 0.71 mmol), at which point the color of the reaction mixture went from golden yellow to a brilliant yellow. The solution was stirred for 2 h and filtered. The filtrate was then concentrated to ca. 2 mL and allowed to sit at −35 °C for 24 h to yield **9c** as yellow crystals in 98.4% yield (0.132 g, 0.35 mmol). ^1H NMR: δ 5.7 (overlapping m, 2 H, $CH_2-CH{=}CH_2$), 4.81 (ddt, 1 H, syn-$CH_2-CH{=}CH_2$-**A**), 4.7 (overlapping ddt, 2 H, $CH_2-CH{=}CH_2$-**B**), 4.60 (ddt, 1 H, anti-$CH_2-CH{=}CH_2$-**A**), 4.09 (m, 1 H, CH_2CHCH_2), 3.05 (ddt, 2 H, anti-CH_2CHCH_2), 2.19 (d d, 2 H, syn-CH_2CHCH_2), 1.32 (m, 2 H, $CH_2-CH{=}CH_2$-**A**), 0.90 (d, 18 H, $^2J_{HP}$ = 8.4 Hz, PMe_3), 0.85 (obscured m, 2 H, $CH_2-CH{=}CH_2$-**B**). $^{13}C\{^1H\}$ NMR: δ 148.68 (m, $^3J_{CP}$ = 3.0 Hz, $CH_2-CH{=}CH_2$), 147.16 (m, $^3J_{CP}$ = 3.3 Hz, $CH_2-CH{=}CH_2$), 116.65 (s, CH_2CHCH_2), 102.57 (s, $CH_2-CH{=}CH_2$), 57.62 (m, $^2J_{CP-trans}$ = 40.7 Hz, CH_2CHCH_2), 17.69 (m, $^1J_{CP}$ = 27.1 Hz, PMe_3), 16.15 (m, $^2J_{CP}$ = 15.8 Hz, $CH_2-CH{=}CH_2$), 14.33(m, $^2J_{CP}$ = 14.0 Hz, $CH_2-CH{=}CH_2$). $^{31}P\{^1H\}$ NMR: δ −7.02 (J_{RhP} = 149.9 Hz).

Preparation of Rh(π-allyl)(P(OPh)$_3$)$_2$ (11). To a room-temperature solution of Rh(allyl)$_3$ (0.0313 g, 0.14 mmol) in 5 mL of toluene was added triphenyl phosphite (0.086 g, 0.28 mmol) with stirring. Approximately 30 min after the phosphite addition, a brilliant yellow precipitate was observed. The reaction mixture was stirred an additional 2 h, during which time the precipitate had dissolved. The filtrate was then concentrated to ca. 2 mL and allowed to sit at −35 °C for 24 h to yield **11** as yellow crystals in 96.7% yield (0.102 g, 0.13 mmol). GC analysis of a portion of this reaction revealed that the organic byproducts were *n*-hexane, 2-methylpentane, and 1-hexene. ^1H NMR: δ 7.55, 6.92 (m. 30 H, Ph), 5.20 (m, 1 H, CH_2CHCH_2), 3.03 (ddt, 2 H, syn-CH_2CHCH_2), 2.51 (ddt, 2 H, anti-CH_2CHCH_2). $^{13}C\{^1H\}$ NMR: δ 148.05 (s, aryl), 124.57 (s, aryl), 119.29 (s, aryl), 117.01 (s, aryl)109.12 (s, CH_2CHCH_2), 51.29 (m, CH_2CHCH_2). $^{31}P\{^1H\}$ NMR: δ −138.54 (J_{RhP} = 328.3 Hz). Anal. Calcd for $C_{39}H_{35}P_2O_6Rh$: C, 61.27; H, 4.61. Found: C, 61.20; H, 4.76.

Preparation of Ir(σ-allyl)$_3$(C≡N-2,6-Me$_2$-C$_6$H$_3$)$_3$ (12). To a room-temperature solution of Ir(allyl)$_3$ (0.100 g, 0.32 mmol) in toluene (10 mL) was added xylylisocyanide (0.125 g, 0.95 mmol). Upon addition of the isocyanide, the reaction mixture immediately turned orange-brown in color and was stirred for 10 min. The reaction mixture was allowed to sit at −35 °C for 24 h to yield **12** as colorless crystals in 84.2% yield (0.143 g, 0.31 mmol). ^1H NMR: δ 6.87 (m, 3 H, $CH_2-CH{=}CH_2$), 6.8−6.6 (9 H, aromatic), 5.11 (ddt, 3 H, anti-$CH_2-CH{=}CH_2$), 4.64 (d d, 3 H, syn-$CH_2-CH{=}CH_2$), 2.64 (d, 6 H, $CH_2-CH{=}CH_2$), 2.26 (s, 18 H, Me). $^{13}C\{^1H\}$ NMR: δ 152.22 (s, $CH_2-CH{=}CH_2$), 139.02 (s, C≡N), 134.94 (s, aromatic), 128.0 (obscured, aromatic), 127.90 (s, aromatic), 104.25 (s, $CH_2-CH{=}CH_2$), 18.96 (s, Me), 14.12 (s, $CH_2-CH{=}CH_2$). IR (mineral oil): 2160 cm^{-1} (s), 2104 (vs), ν(C≡N); 1616 cm^{-1} (vw), ν(C=C). Anal. Calcd for $C_{27}H_{30}PIr$: C, 60.99; H, 5.97; N, 5.93. Found: C, 60.72; H, 6.14; N, 6.11.

Reaction of Rh(allyl)$_3$ with C≡N-2,6-Me$_2$C$_6$H$_3$. This reaction was set up in the same manner as that for **12**. Upon addition of the isocyanide, the golden-yellow color of Rh(allyl)$_3$ quickly turned to dark brown. Attempts to isolate a Rh complex from this reaction were unsuccessful. GC/MS analysis

Table 1. Crystal Data and Data Collection and Refinement Parameters for M(allyl) Complexes

	6	7	8	9a	12
empirical formula	$C_{54}H_{60}Ir_2P_2$	$C_{45}H_{39}IrP_2 \cdot 2(C_7H_8)$	$C_{43}H_{48}IrP_3 \cdot (C_7H_8)$	$C_{15}H_{33}IrP_2$	$C_{36}H_{42}IrN_3$
fw	1155.36	946.17	849.92	467.55	708.93
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P2_1/c$
a, Å	9.2972(4)	10.7816(5)	11.2226(5)	8.3600(4)	10.9408(5)
b, Å	15.7287(7)	13.5959(6)	25.4429(13)	27.2735(13)	14.6602(7)
c, Å	16.6995(8)	13.9441(6)	16.3141(8)	9.0323(4)	20.4426(9)
α, deg	73.249(1)	86.058(1)	90	90	90
β, deg	82.344(1)	71.302(1)	106.450(1)	115.491(1)	98.025(1)
γ, deg	79.303(1)	83.341(1)	90	90	90
V, Å^3	2289.49(18)	1921.98(15)	4467.6(4)	1858.94(15)	3246.8(3)
ρ_{calcd}, g cm^{-3}	3.352	1.441	1.264	1.671	1.450
Z	4	2	4	4	4
μ, mm^{-1}	11.824	3.586	3.121	7.340	4.139
λ(Mo Kα), Å	0.71073	0.71073	0.71073	0.71073	0.71073
T, K	203	203	203	203	203
GooF[a]	0.999	1.003	1.023	1.396	1.027
*R*1 [$I > 2\sigma(I)$], %[b]	2.62	2.74	2.92	4.97	3.51
*wR*2 [$I > 2\sigma(I)$], %[c]	6.45	7.50	7.33	11.28	6.89
*R*1 (all data), %[b]	3.19	3.10	3.92	5. 57	5.54
*wR*2 (all data), %[c]	6.70	7.67	7.61	11.49	7.49
lrgst diff peak/hole, e Å^{-3}	1.940 and −1.670	0.574 and −0.408	1.136 and −1.018	3.049 and −3.803	0.862 and −0.789

[a] GooF = $[\sum[w(F_o^2 - F_c^2)]^2/(n-p)]^{1/2}$; n = number of reflections, p = total number of parameters refined. [b] $R1 = \sum|F_o| - |F_c|/\sum|F_o|$. [c] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]^{1/2}$.

of a portion of this reaction revealed that CH_2=$CHCH_2$-C(=N-2,6-$Me_2C_6H_3$)C(=N-2,6-$Me_2C_6H_3$)CH_2CH=CH_2 had been generated (the analogous organic product was observed for the reaction of Rh(allyl)$_3$ with CN^{t}Bu).

Generation of Ir(*σ*-allyl)$_3$(CO)$_3$ (13). To a two-neck round-bottom flask fitted with a balloon was added Ir(allyl)$_3$ (0.088 g, 0.28 mmol), toluene-d_8 (5 mL), and carbon monoxide (ca. 1.5 atm). Aliquots were removed from the reaction flask periodically for NMR and IR analysis. It was found that all the Ir(allyl)$_3$ had been consumed after 26 h. NMR analysis revealed that conversion to Ir(*σ*-allyl)$_3$(CO)$_3$ was quantitative. Vacuum workup of the reaction mixture resulted in formation of a mixture of **13** and presumably Ir(*σ*-allyl)$_2$(*π*-allyl)(CO)$_2$ (**14a**). Formation of the latter complex is reversible (no other products are observed by NMR), and addition of CO results in clean conversion of **14a** back to **13**. ^{1}H NMR: *δ* 6.16 (m, 3H, CH_2-CH=CH_2), 4.84 (ddt, 3H, anti-CH_2-CH=CH_2), 4.54 (dd, 3H, syn-CH_2-CH=CH_2), 2.01 (d, 6H, CH_2-CH=CH_2). ^{13}C{^{1}H} NMR: *δ* 163.77 (s, *C*O), 147.34 (s, CH_2-CH=CH_2), 109.67 (s, CH_2-CH=CH_2), 15.41 (s, CH_2-CH=CH_2). IR (toluene): 2067(vs), 2121(m) cm^{-1} (s), *ν*(C≡O); 1622 cm^{-1} (vw), *ν*(C=C).

^{1}H NMR for **14a**: *δ* 6.34 (m, 2H, CH_2-CH=CH_2), 4.90 (ddt, 2H, syn-CH_2-CH=CH_2), 4.59 (ddt, 2H, anti-CH_2-CH=CH_2), 4.03 (m, 1 H, CH_2CHCH_2), 3.75 (ddt, 2H, syn-CH_2CHCH_2), 1.9 (obscured m, 4H, CH_2-CH=CH_2), 1.55 (ddt, 2H, anti-CH_2-CHCH_2). IR (neat): 2018(vs), 2054(m) cm^{-1}, *ν*(C≡O).

Generation of Rh(*σ*-allyl)$_2$(*π*-allyl)(CO)$_2$ (14b). Addition of CO to Rh(allyl)$_3$ in the same manner as for **13** generated Rh(*σ*-allyl)$_2$(*π*-allyl)(CO)$_2$, **14b.** Vacuum workup of the solution led to significant decomposition and afforded as yet uncharacterized Rh products. GC analysis of a portion of this reaction revealed that allylaldehyde had been generated. ^{1}H NMR: *δ* 5.79 (m, 2H, CH_2-CH=CH_2), 4.94 (ddt, 2H, syn-CH_2-CH=CH_2), 4.84 (ddt, 2H, anti-CH_2-CH=CH_2), 4.65 (m, 1 H, CH_2CHCH_2), 3.60 (ddt, 2H, syn-CH_2CHCH_2), 2.64 (d, 4H, CH_2-CH=CH_2), 1.53 (ddt, 2H, anti-CH_2CHCH_2). ^{13}C{^{1}H} NMR: *δ* 191.02 (s, *C*O), 131.48 (m, CH_2CHCH_2), 118.9 (overlapping m, CH_2-CH=CH_2), 60.39 (m, CH_2CHCH_2), 47.1 (overlapping m, CH_2-CH=CH_2), 30.14 (overlapping m, CH_2-CH=CH_2). IR (toluene): 1988 (vs), 2050 (m) cm^{-1}, *ν*(C≡O); 1618 cm^{-1} (vw), *ν*(C=C).

Generation of Ir(*σ*-allyl)$_3$(CO)$_2$PMe$_3$ (15). An aliquot was taken from the reaction used to generate **13** (roughly 1/3 of the total volume; ca. 0.09 mmol). To this sample was added PMe_3 (46 mL, 0.45 mmol), and the sample was stirred for 1 h. NMR analysis revealed that the conversion to **15** was quantitative. ^{1}H NMR: *δ* 6.67 (m, 1H, CH_2-CH=CH_2), 6.31 (m, 2H, CH_2-CH=CH_2), 5.12 (ddt, 1H, anti-CH_2-CH=CH_2), 4.82 (ddt, 2H, anti-CH_2-CH=CH_2), 4.70 (ddt, 1H, syn-CH_2-CH=CH_2), 4.63 (ddt, 2H, syn-CH_2-CH=CH_2), 4.65 (m, 1 H, CH_2CHCH_2), 2.49 (m, 2H, CH_2-CH=CH_2), 1.75 (overlapping m, 4H, CH_2-CH=CH_2), 0.80 (s, 9H, PMe_3). ^{13}C{^{1}H} NMR: *δ* 169.12 (s, 2C, *C*O), 149.35 (s, 1C, CH_2-*C*H=CH_2), 148.27 (s, 2C, CH_2-CH=CH_2), 107.20 (s, 2C, CH_2-CH=*C*H_2), 106.30 (s, 1C, CH_2-CH=*C*H_2), 16.80 (2, 1C, *C*H_2-CH=CH_2, $^2J_{PC}$ = 51.9 Hz), 15.39 (s, 2C, *C*H_2-CH=CH_2, $^2J_{PC}$ = 5.8 Hz), 14.37 (s, 3C, PMe_3, $^1J_{PC}$ = 30.7 Hz). ^{31}P{^{1}H} NMR: *δ* −61.38. IR (benzene): 2011 (m, br), 2065 (vs) cm^{-1}, *ν*(C≡O).

Single-Crystal X-ray Diffraction Studies. Single-crystal X-ray diffraction experiments were performed on a Bruker P4/CCD/PC diffractometer with graphite-monochromated Mo Kα radiation (*λ* = 0.71073 Å). Diffraction data were refined using SHELXTL PC.[12] Single crystals of **6**, **7**, **8**, **9a**, and **12** were grown from concentrated toluene solutions at room temperature. Crystals were coated in mineral oil and mounted on a glass fiber at −70 °C.

A hemisphere of data was collected using a combination of *ϕ* and *ω* scans, with 30 s frame exposures and 0.3° frame widths. Data collection and initial indexing and cell refinement were performed using SMART[13] software. Frame integration and final cell parameter calculations were carried out using SAINT[14] software. The data were corrected for absorption using the SADABS[15] program. Decay of reflection intensity was not observed. The crystal and refinement parameters are listed in Table 1. Average bond distances and angles are listed in Table 2.The structures were solved using difference Fourier techniques. The initial solutions revealed Ir and the majority of all other non-hydrogen positions. The remaining atomic positions were determined from subsequent Fourier syntheses. All hydrogen atom positions were fixed in ideal positions. The C−H distances were fixed at 0.93 (aromatic), 0.96 (methyne), 0.97 (methylene), and 0.98 Å (methyl). The hydrogen atoms were refined using a riding model, with their isotropic temperature factors set to 1.2 (aromatic, methyne, methylene) or 1.5 (methyl) times the isotropic *U* of the carbon atom they were bonded to.

(12) *SHELXTL Version 5.1*; Bruker Analytical X-Ray Systems: 6300 Enterprise Lane, Madison, WI 53719, 1997.
(13) *SMART Version 4.210*; Bruker Analytical X-Ray Systems: 6300 Enterprise Lane, Madison, WI 53719, 1996.
(14) *SAINT Version 4.05*; Bruker Analytical X-Ray Systems: 6300 Enterprise Lane, Madison, WI 53719, 1996.
(15) *SADABS*; George Sheldrick, University of Göttingen, Germany, 1996.

Table 2. Average Bond Distances (Å) and Angles (deg) for M(allyl) Complexes[a,b]

nuclei	6	7	8	9a	12
M−C1	2.167[4]	2.190[2]	2.198[4]	2.22[1]	2.160[5]
M−C4(C6)	2.217[5]	2.236[2]	NA	2.23[1]	NA
M−C5	2.145[5]	2.186(2)	NA	2.18(1)	NA
C2−C3	1.36[1]	1.318[4]	1.311[4]	1.34[2]	1.25[1]
C1−C2−C3	130[1]	127.2(3)	127.0[5]	126[1]	136[2]
C4−C5−C6	119.2[5]	121.1[3]	NA	122.1(7)	NA
M−L	2.311[1]	2.2783[6]	2.324[1]	2.282[1]	1.979[5]

[a] Esd's (standard deviations) are given in parentheses. Values in square brackets are arithmetic means of esd's. [b] All σ- and π-allyl bond distances and angles have been averaged, with σ-allyls being designated by C1−3 and π-allyls by C4−6.

Ir(σ-allyl)(π-allyl)$_2$(PPh$_3$) (6). Crystals of **6** were shown to adopt the space group $P\bar{1}$ with two molecules observed in the asymmetric unit. Refinement revealed that the central carbon (C2) of the σ-allyl group was disordered over two sites. The disorder was modeled by refining the carbon atoms with a shared free variable that assigned the occupation of the sites on the basis of the observed electron density.

Ir(σ-allyl)$_2$(π-allyl)(Ph$_2$PC$_6$H$_4$PPh$_2$) (7). Crystals of **7** were shown to adopt the space group $P\bar{1}$. Very disordered toluene molecules were observed in the lattice of **7**, and the program PLATON/SQUEEZE was used to remove the toluene solvent electron density.[16] The solvent volume modeled for **7** consisted of two sites centered at 0.5, 0.75, 0.75 and 0.5, 0.25, 0.25 in the unit cell. The solvent volume modeled was 369 Å^3, and 100 electrons per unit cell were removed.

Ir(σ-allyl)$_3$[Ph$_2$P(CH$_2$)$_2$P(Ph)(CH$_2$)$_2$PPh$_2$] (8). Crystals of **8** were shown to adopt the space group $P2_1/n$. Like **7**, severely disordered toluene was observed in the lattice of **8**. The solvent volume modeled for **8** consisted of two sites centered at 0.0, 0.5, 0.0 and 0.0, 1.0, 0.5 in the unit cell. The solvent volume modeled was 1056 Å^3, and 456 electrons per unit cell were removed. Further refinement of **8** revealed that the terminal carbon atom (C9) of the σ-allyl group was disordered over two sites. The disorder was modeled by refining the carbon atoms with a shared free variable that assigned the occupation of the sites on the basis of the observed electron density.

Ir(σ-allyl)$_2$(π-allyl)(PMe$_3$)$_2$ (9a). Crystals of **9a** were shown to adopt the space group $P2_1/n$. Refinement revealed that the central carbon (C8) of the σ-allyl group was disordered over two sites. The disorder was modeled by refining the carbon atoms with a shared free variable that assigned the occupation of the sites on the basis of the observed electron density.

Ir(σ-allyl)$_3$(C≡N-2,6-Me$_2$C$_6$H$_3$) (12). The refinements of **12** occurred in a straightforward manner. No disorder was observed.

Results

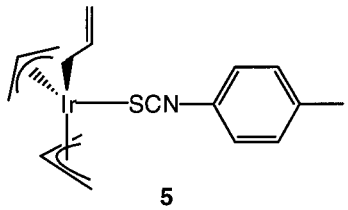
M(allyl)$_3$ Synthesis. The literature procedure for preparing Ir(allyl)$_3$ (**3**) from Ir(acac)$_3$ (acac = acetylacetonate) and (allyl)MgCl affords the desired product in ca. 20% yield.[4] Given the similarly low yield for the preparation of Ir(acac)$_3$ from commercial precursors, a new synthetic approach was called for. Wilkinson and co-workers have reported that the homoleptic methyl complex [Li(tmeda)]$_3$[IrMe$_6$] can be prepared in over 90% yield from the interaction of IrCl$_3$(tht)$_3$ (**1**; tht = tetrahydrothiophene) with methyllithium.[17] We have found that crystalline *mer*-IrCl$_3$(tht)$_3$ can be prepared from IrCl$_3$(H$_2$O)$_x$ in ca. 90% yield via a slight modification of the original synthesis.[10] Reaction of IrCl$_3$(tht)$_3$ with allyllithium in benzene affords Ir(allyl)$_3$ in >80% NMR yield (eq 1).

$$IrCl_3(tht)_3 + 3\ LiC_3H_5 \xrightarrow[25\ °C]{\text{benzene}} Ir(C_3H_5)_3 + 3\ LiCl + 3\ tht \quad (1)$$

Attempts to isolate the product from this method have not provided Ir(allyl)$_3$ in comparable yields (less than 30%); however, use of more volatile solvents such as Et$_2$O afford sublimed, microcrystalline product in over 47% yield.

The preparation of Rh(allyl)$_3$ can be achieved via the same method utilized in the synthesis of the Ir analogue, although the isolated yield is much higher (ca. 86%). This method is thus comparable with the synthesis reported by Powell and Shaw from RhCl$_3$(H$_2$O)$_x$ and allylMgBr.[7]

Reactions of M(allyl)$_3$ with N, O, and S donors. The tris(allyl) complexes were surprisingly unreactive toward typical N, O, and S donor ligands. Pyridine, trialkylamines, anilines (aniline, 3,5-bis(trifluoromethyl)aniline), diimines (bipyridine, *o*-phenanthroline), and acetonitrile all showed no irreversible binding after days at 25 °C. Similar results were obtained for ethers (Et$_2$O, thf), alcohols (MeOH, ^{t}BuOH, PhOH, Ph$_3$SiOH), and acetone. Even "soft" S donors such as phenylthiol, thioethers (tht, [PhS(CH$_2$)]$_2$), and thiocamphor were unreactive. However, addition of tolylisothiocyanate to Ir(allyl)$_3$ provided Ir(σ-allyl)(π-allyl)$_2$(SCN-Tol) (**5**) in moderate yield after stirring for 3 days at 20 °C. No reaction was observed between Rh(allyl)$_3$ and Tol-NCS. The composition of **5** was established by ^{1}H and ^{13}C NMR analysis, which revealed the presence of one σ-allyl and two *inequivalent* π-allyl groups in an unsymmetrical structure. Although thiocamphor may be too



5

sterically bulky to give a stable adduct, "soft" donors appeared to be favored by the tris(allyl) complexes, so we investigated their reactivity toward a variety of readily accessible phosphorus donors.

P-Donors. Treatment of isolated Ir(allyl)$_3$ with PPh$_3$ in toluene gives the 1:1 adduct Ir(σ-allyl)(π-allyl)$_2$(PPh$_3$) **6** in high yield.[8] Alternatively, the hexane filtrate from the synthesis of Ir(allyl)$_3$ can be used directly to prepare **6** with comparable efficiency. Complex **6** did not react further with excess PPh$_3$, even at 100 °C. The infrared spectrum of **6** displays a characteristic C=C stretch in the 1600−1610 cm^{-1} region due to the σ-allyl group.[18] The ^{1}H and ^{13}C NMR spectra of **6** established the presence of one σ-allyl and two *inequivalent* π-allyl groups (Figure 1), even at 100 °C. The PPh$_3$ ligand is located trans to a methylene group of one of the π-allyl groups, as evidenced by the large P−C coupling constant

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(17) (a) Hay-Motherwell, R. S.; Wilkinson, G.; Hussain, B.; Hursthouse, M. B. *J. Chem. Soc., Chem. Commun.* **1989**, 1436. (b) Hay-Motherwell, R. S.; Wilkinson, G.; Hussain-Bates, B.; Hursthouse, M. B. *Polyhedron* **1990**, *9*, 2071.

(18) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; Wiley: New York, 1997.

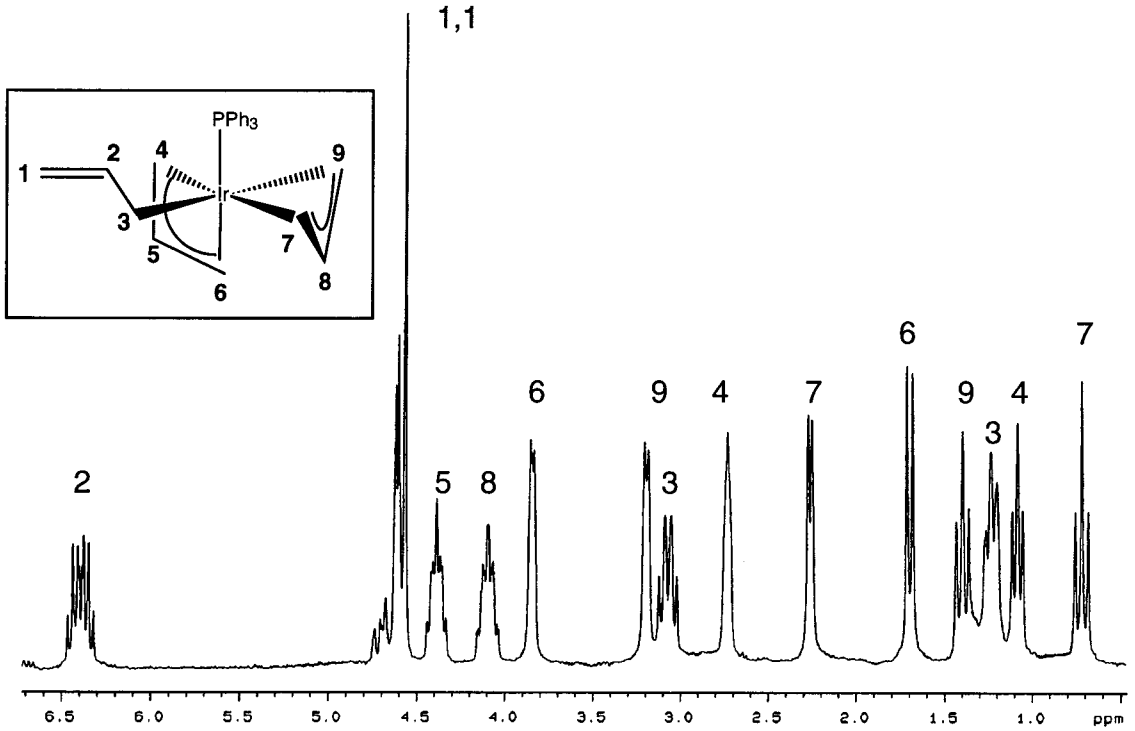
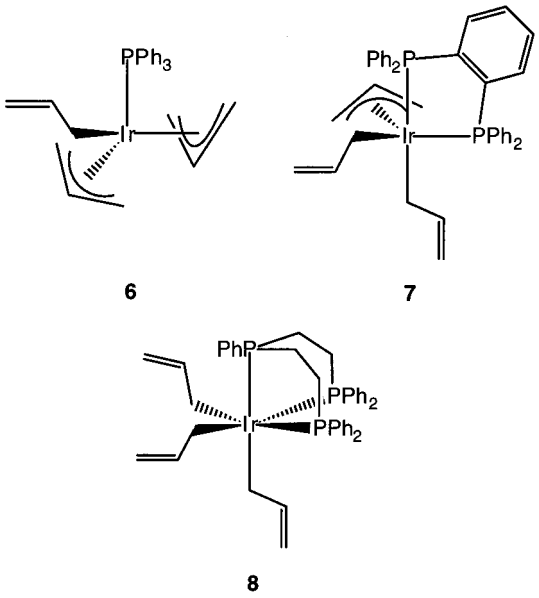


Figure 1. ^{1}H NMR of **6**.

($^2J_{PC}$ = 38 Hz). This was further confirmed by an X-ray crystallographic study of **6** (Figure 2), which shows the



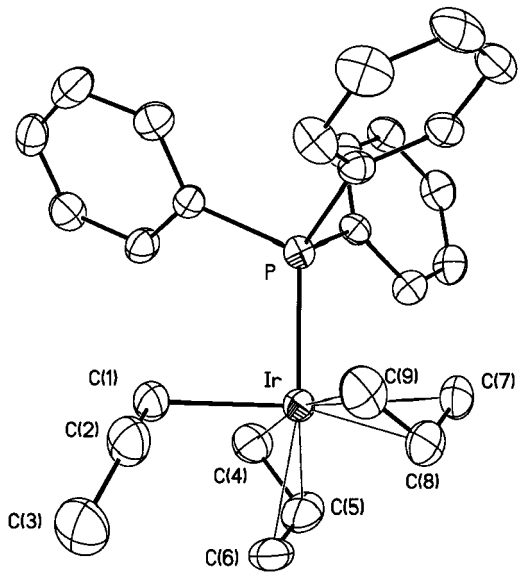


Figure 2. Thermal ellipsoid representation of **6** shown at the 50% probability level. Hydrogen atoms have been omitted for clarity. Only 1 of the 2 molecules in the asymmetric unit is shown. Only one orientation of the disordered allyl group is shown (see the Experimental Section).

π-allyl ligand trans to P is symmetrically bound with typical Ir−C bond distances[19] (Ir−CH = 2.145[5], Ir−CH_2 = 2.217[5] Å). The other π-allyl ligand is unsymmetrically bound as a result of the trans influence of the σ-allyl {C(1)−Ir−C(7) = 161.6[2]°, Ir−C(7) = 2.268[4] vs Ir−C(9) = 2.196[4] Å}. The upfield shift of the methylene protons induced by the trans P (or S) and σ-allyl groups allowed us to assign all 15 inequivalent allyl proton resonances (see Experimental Section) for both **5** and **6**.

Addition of the chelating bis(phosphine) 1,2-$(PPh_2)_2$-C_6H_4 to Ir(allyl)$_3$ affords Ir(σ-allyl)$_2$(π-allyl)(1,2-$(PPh_2)_2$-C_6H_4) **7** in good yield. Complex **7** has inequivalent σ-allyl groups as determined by NMR analysis, even at 100 °C, with the two phosphorus donors trans to one methylene of the π-allyl ($^2J_{PC}$ = 39.4 Hz) and to one of the σ-allyl groups ($^2J_{PC}$ = 79.5 Hz), respectively. The cis geometry of the σ-allyl groups was confirmed by X-ray structural analysis (Figure 3). Like **6**, the structure of **7** reveals that there is a significant trans influence by one of the σ-allyl groups on the single π-allyl group [C(1)−Ir−C(7) = 162.1(1)°, Ir−C(7) = 2.270(2) vs Ir−C(9) = 2.202(3) Å].

(19) Manger, M.; Wolf, J.; Teichert, M.; Stalke, D.; Werner, H. *Organometallics* **1998**, *17*, 3210.

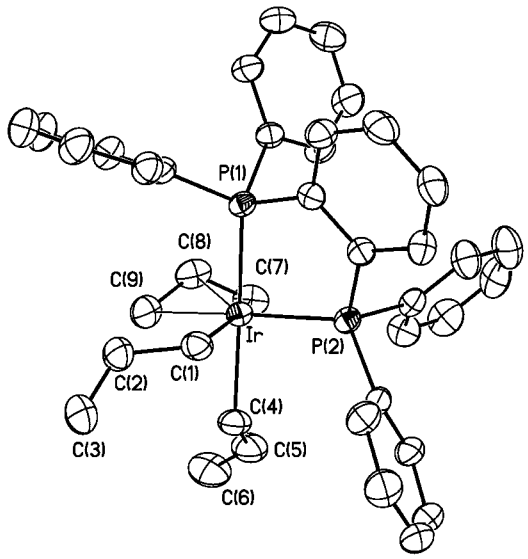


Figure 3. Thermal ellipsoid representation of **7** shown at the 50% probability level. Hydrogen atoms have been omitted for clarity.

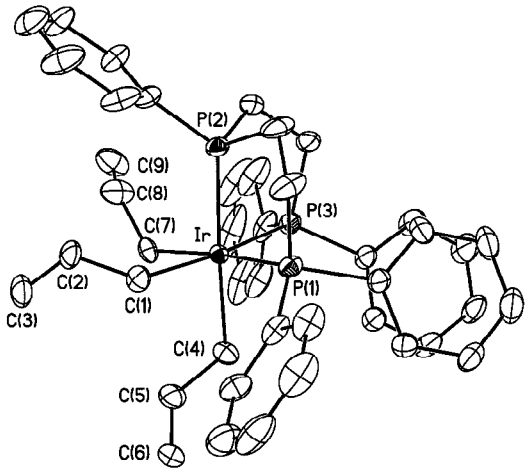


Figure 4. Thermal ellipsoid representation of **8** shown at the 50% probability level. Hydrogen atoms have been omitted for clarity. Only one orientation of the disordered allyl group is shown (see the Experimental Section).

Addition of the tridentate phosphine $PhP(CH_2CH_2PPh_2)_2$ to $Ir(allyl)_3$ gives tris(σ-allyl) complex **8**. This triphos complex has two sets of σ-allyl groups in a 1:2 ratio, consistent with C_s symmetry. X-ray structural analysis of **8** (Figure 4) reveals that there is a significant difference in the bond distances associated with the terminal and central Ir−P bonds (2.339[1] and 2.294(1) Å, respectively). This difference is not observed in the corresponding σ-allyl groups, and the esd's on the Ir−C bonds preclude further discussion. Less bulky phosphorus ligands such as PMe_3 and $P(OPh)_3$ react with $Ir(allyl)_3$ to afford $IrL_2(\sigma\text{-allyl})_2(\pi\text{-allyl})$ (**9a**,**b**) in high yield. NMR analysis of **9a**,**b** indicated that, in contrast with **7**, the *inequivalent* σ-allyl ligands are trans to one another. In particular, we observe overlapping methyne proton resonances for the σ-allyl ligands at δ 5.8 and significant phosphorus coupling to both methylene carbons of the π-allyl group (av $J_{CP} = 32.6$ Hz). Proton resonances due to the inequivalent σ-allyl ligands in **9a**,**b** all broaden at higher temperatures, but we were unable to reach a well-defined coalescence

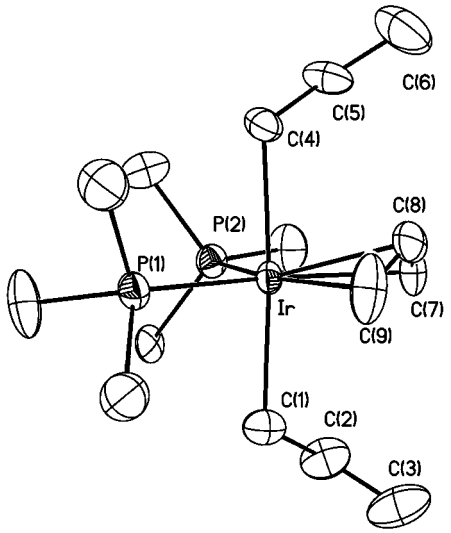
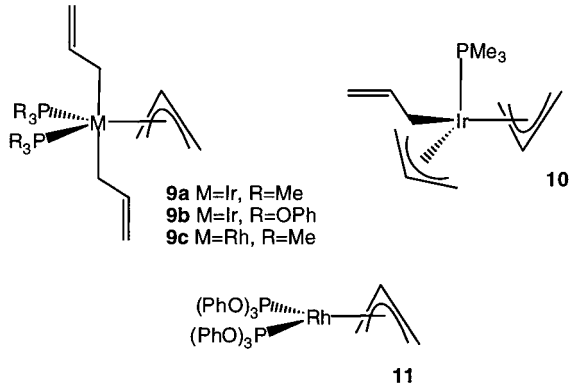


Figure 5. Thermal ellipsoid representation of **9a** shown at the 50% probability level. Hydrogen atoms have been omitted for clarity. Only one orientation of the disordered σ-allyl group is shown (see the Experimental Section).

temperature below their decomposition points. Conversely, the single ^{31}P resonance for each of **9a** and **9b**

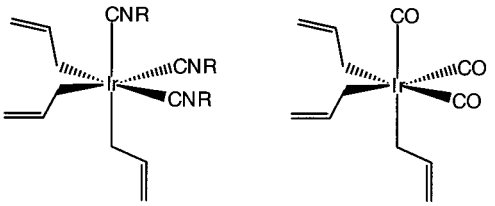


did not undergo sufficient broadening at −80 °C for us to estimate the activation barrier for this fluxional process. The trans configuration in **9a**,**b** was further confirmed through single-crystal X-ray diffraction analysis (Figure 5).[20] Attempts to isolate a mono-PMe_3 complex have not been successful. Addition of 1 equiv of PMe_3 to $Ir(allyl)_3$ results in the formation of a mixture containing the parent tris(allyl)iridium, **9a**, and presumably $Ir(\sigma\text{-allyl})(\pi\text{-allyl})_2(PMe_3)$ **10**. A single ^{31}P NMR resonance for **10** appears at −44.5 ppm, and the ^1H NMR spectrum is similar to that observed for the PPh_3 analogue **6**. Furthermore, addition of a 10-fold excess of PMe_3 provides only **9a** even after heating (85 °C, 24 h). Attempts to prepare the Rh analogues of complexes **6**−**8** were unsuccessful. In the case of triphenylphosphine, we were able to isolate the previously reported Rh(I) species, $Rh(\pi\text{-allyl})(PPh_3)_2$, in rather low yield (less than 10%). This compound has been prepared previously from a refluxing methanol solution of $Rh(allyl)_3$ and PPh_3 in 85% yield.[7] A similar reaction with $P(OPh)_3$

(20) While the structural analysis of **9a** confirmed the proposed structure, the refinement was only fair, as was that of the phosphite complex **9b**. Full details for **9a**,**b** are provided in the Supporting Information.

gave a higher yield of analogous **11**, in addition to the C_6 organic products, hexane, hexene, and 2-methylpentane. In contrast, Rh(allyl)$_3$ and the powerful donor PMe_3 provided the trivalent Rh complex of Rh(σ-allyl)$_2$(π-allyl)(PMe_3)$_2$ (**9c**) in good yield. The formulation of **9c** was based on the similarity of its NMR spectrum to that of **9a**. There was no evidence to suggest the formation of any Rh(I) species. Specifically, ^{31}P NMR analysis reveals that the rhodium−phosphorus coupling is approximately 150 Hz (cf. 200 Hz for Rh(π-allyl)(PPh_3)$_2$), indicative of a Rh(III) species.[21] The PMe_3 complexes thus constitute the only isostructural pair of Ir/Rh-tris(allyl) adducts observed to date.

C-Donors. As with phosphorus donors, we observe significant reactivity differences between tris(allyl)-rhodium and -iridium with C-donor ligands. Addition of xylylisocyanide to Ir(allyl)$_3$ provides Ir(σ-allyl)$_3$(CN-2,6-$Me_2C_6H_3$)$_3$ (**12**) in high yield. The geometry of the



12

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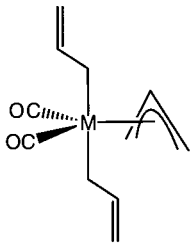


14a M=Ir
14b M=Rh

tris-isocyanide complex is *fac*, as evidenced by the lone set of σ-allyl resonances in the ^{1}H NMR. Furthermore, IR analysis reveals two CN stretches at 2160 and 2104 cm^{-1} (presumably of a_1 and e symmetry, respectively) consistent with pseudooctahedral C_{3v} symmetry.[18] This is borne out by the structural analysis of **12** (Figure 6), which shows the *fac*-geometry with essentially linear M−CNR fragments ($\angle$(Ir−C≡N) = 177.3[4]°; $\angle$(C≡N−C_{xylyl}) = 173.7[5]°). Also of note is the significant difference in the Ir−C_{allyl} bond distances between compound **12** (av 2.160[5] Å) and triphos derivative **8** (av 2.198[4] Å). This difference directly reflects the superior σ-donor strength and trans influence of the triphos ligand relative to isocyanides. Addition of isocyanides to Rh(allyl)$_3$ results in the initial formation of a tris-σ-allyl complex (as observed by ^{1}H NMR), which quickly (less than 5 min) decomposes at room temperature via reductive elimination to provide as yet uncharacterized metal-containing products. GC/MS analysis of the organic products revealed the formation of an α-diimine

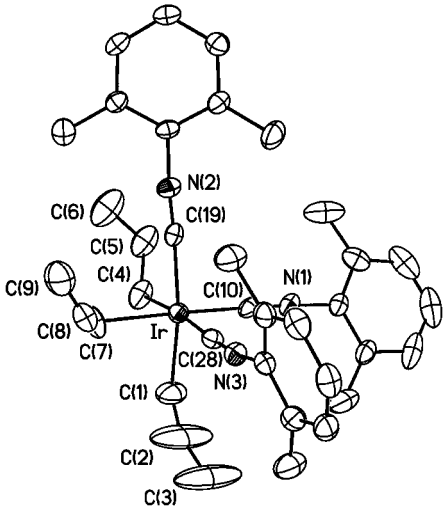
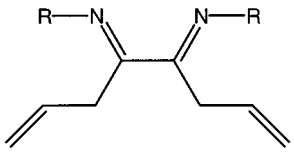


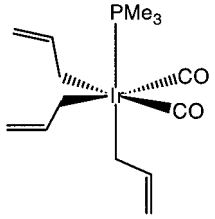
Figure 6. Thermal ellipsoid representation of **12** shown at the 50% probability level. Hydrogen atoms have been omitted for clarity.

(CH_2=$CHCH_2C$(=NR)C(=NR)CH_2CH=CH_2; R = cyclohexyl, ^{t}Bu, xylyl) that presumably forms via insertion of an isonitrile into the Rh−C_{allyl} bond followed by reductive elimination.



Addition of carbon monoxide to M(allyl)$_3$ generates Ir(σ-allyl)$_3$(CO)$_3$ (**13**) and Rh(σ-allyl)$_2$(π-allyl)(CO)$_2$ (**14b**), respectively. Vacuum workup of **13** results in the formation of a mixture of **13** and Ir(σ-allyl)$_2$(π-allyl)(CO)$_2$ (**14a**), as evidenced by the similarity of the ^{1}H NMR to **14b**. The formation of **14a** appears to be reversible, as CO exposure regenerates pure **13** in nearly quantitative yield. Removal of solvent under vacuum from product **14b** results in the insertion of CO into the Rh−allyl bond followed by reductive elimination to yield allylaldehyde and as yet uncharacterized organometallic products.

Studies of the reactivity of the aforementioned carbonyl complexes are currently underway. Preliminary studies indicate that both **13** and **14b** are reactive toward phosphines. For instance, **13** reacts with PMe_3 to provide the monophosphine adduct Ir(σ-allyl)$_3$(CO)$_2$$PMe_3$ (**15**) in quantitative yield. This reactivity is



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consistent with the fact that **13** reversibly loses a CO to form **14a**. Attempts to isolate a mixed carbonyl/phosphine complex from **14b** have so far been unsuc-

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cessful. It appears that addition of PMe_3 to **14b** results in a rapid equilibrium between **14b** and a product analogous to **15**, as evidenced by ^1H and ^{31}P NMR.

Discussion

Although allyllithium is not typically the reagent of choice for preparing transition metal allyl complexes,[1e] we have been unable to obtain high yields of tris(allyl)-iridium (**3**) using magnesium or tin reagents. The $M(allyl)_3$ product is particularly sensitive to heat as a solid or in concentrated solution, although we have not characterized its decomposition reaction or the resulting insoluble brown residue in detail. As a result, the crude hexane extracts of **3** are often the preferred starting material for investigating its chemistry. Similar problems are not encountered for the Rh analogue, which can be purified by sublimation in high yield, although solutions cannot be heated much above 60 °C without noticeable decomposition.

The ligand addition chemistry of $M(allyl)_3$ is remarkably selective for "soft" donors. Such is not the case for the 16 e^- group 10 bis(allyl) complexes, for which the NMR spectra are highly solvent dependent due to facile dynamic $\pi-\sigma$ allyl conversion in donor solvents.[22] $Pd(allyl)_2$ reacts readily with alcohols, and diethylamine, for example, gives the amido-bridged dimer.[23] While $Rh(allyl)_3$ reacts readily with the O−H functions of solid metal oxides, no reaction is observed with Ph_3SiOH in the absence of an ancillary donor ligand such as a phosphine.[24]

The structural rigidity of Ir(σ-allyl)(π-allyl)$_2$(PPh_3) (**6**) in solution is likely a result of strong Ir−C bonds and the saturated electron count, i.e., a second $\pi-\sigma$ allyl conversion would be required in the transition state for allyl exchange. For the 16 e^- group 10 homologues, M(σ-allyl)(π-allyl)(PMe_3), no additional coordination site is required and allyl proton exchange barriers are reported to be 9.6 ± 1.5 and 21.1 ± 1.5 kcal/mol for Pd and Pt, respectively.[25] Allyl exchange is also observed for both PPh_3 analogues,[26,27] whereas in the case of the bulkier tricyclohexylphosphine complexes, allyl exchange was observed for the Pd complex, but not for the Pt analogue, even at 90 °C.[28] The steric bulk of **6** is apparent from both its molecular structure in the solid state and its reluctance to add a second phosphine.

The formation of isomeric bis(ligand) tris(allyl)iridium adducts can also be attributed to steric constraints. While the ^1H NMR spectrum of the Rh and Ir dicarbonyl adducts **14a**,**b** are indicative of C_s symmetry, the bis-(PMe_3) complexes **9a**,**c** both exhibit unsymmetrical structures, due presumably to hindered rotation about the M−C bonds of the σ-allyl groups. With the larger arylated bis(phosphine), the trans structure is presumably no longer sterically viable for **7** and the σ-allyl groups adopt the cis orientation.

The redox stability of the heavier group 9 tris(allyl) complexes parallels that of their group 10 homologues. Pd(σ-allyl)(π-allyl)(PPh_3) eliminates 1,5-hexadiene above 0 °C to give the monovalent, allyl-bridged dimer, [Pd(PPh_3)(μ-allyl)]$_2$,[27] and excess phosphine gives $Pd(PPh_3)_4$. In contrast, ligand-induced hydrocarbon elimination from $Pt(allyl)_2$ has not been reported. In our work, only the powerful donor phosphine PMe_3 is capable of stabilizing trivalent tris(allyl)rhodium complexes; the dicarbonyl adduct can be generated in solution, but removal of the solvent in vacuo induces elimination of allylaldehyde.

Conclusion

Reactions of tris(allyl)iridium with "soft" donor ligands afford a variety of trivalent adducts all containing σ-allyl groups. The increased reactivity of the Ir−C bond in these products (relative to $Ir(allyl)_3$) will be especially useful for our future efforts to prepare bis(allyl)iridium-(III) moieties bonded to metal oxide surfaces.[24] We foresee that the increased thermal and redox stability of these supported organoiridium centers may lead to useful catalytic properties for hydrocarbon functionalization reactions.

Acknowledgment. We thank the Department of Energy's Laboratory Directed Research and Development (LDRD) program for financial support and Dr. David C. Smith for preliminary work on the $Ir(allyl)_3$ synthesis.

Supporting Information Available: Tables of all atomic coordinates, anisotropic thermal parameters, bond lengths and bond angles, and hydrogen atom coordinates for **6**, **7**, **8**, **9a**, and **12**. This material is available free of charge via the Internet at http//pubs.acs.org.

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