

Chemistry of M(allyl)₃ (M = Rh, Ir) compounds: structural characterization of tris(allyl)iridium complexes with phosphorus ligands†

Kevin D. John,^a Kenneth V. Salazar,^b Brian L. Scott,^a R. Thomas Baker^{*a} and Alfred P. Sattelberger^{*a}

^a Los Alamos Catalysis Initiative, Chemical Science and Technology Division, Los Alamos National Laboratory, MS J514, Los Alamos, NM 87545, USA. E-mail: weg@lanl.gov; sattelberger@lanl.gov

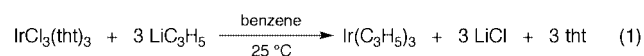
^b Materials Science and Technology Division, Los Alamos National Laboratory, MS E549, Los Alamos, NM 87545, USA

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While addition of phosphorus ligands such as P(OPh)₃ to Rh(allyl)₃ gives monovalent Rh(allyl)L₂, the iridium analog gives stable mixed σ/π-tris(allyl) complexes, as evidenced by the structural characterization of mono-, bi-, and tri-dentate ligand complexes.

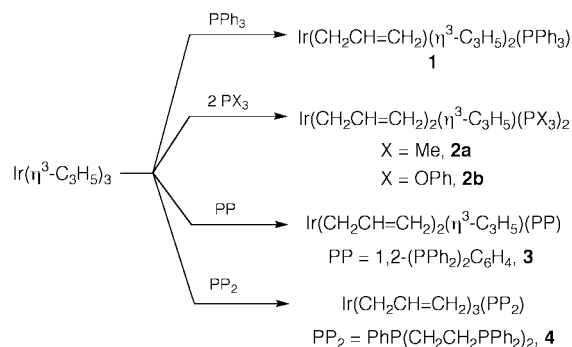
Recent efforts aimed at preparing and characterizing 'single-site' catalysts consisting of well defined, metal-oxide surface-bound, ligated transition metals have yielded exciting new catalytic systems for alkane metathesis and polyolefin depolymerization.^{1,2} One particularly well-characterized class of such sites is derived from reactions of tris(allyl)rhodium, Rh(C₃H₅)₃, with carefully prepared, high-purity metal oxides.^{3–5} The use of these systems for catalysis, however, is hampered by weak Rh–O bonds to the metal oxide surface and the proclivity of trivalent rhodium intermediates to undergo reductive elimination.⁶ We are investigating the use of tris(allyl)iridium to prepare single-site catalysts with better thermal and reductive stability. In expanding the relatively unexplored⁷ ligand addition chemistry of M(allyl)₃ compounds, we have developed an improved synthesis of the iridium analog and demonstrated that its reactions with a variety of phosphorus ligands all afford trivalent products, including a stable tris(σ-allyl) adduct.

The literature procedure⁸ for preparing Ir(allyl)₃ from Ir(acac)₃ (acac = acetylacetonate) and (allyl)MgCl affords the desired product in ca. 20% yield. Ir(acac)₃ is itself prepared in ca. 10% yield from commercially available IrCl₃·xH₂O. We have found that the crystalline yellow tetrahydrothiophene adduct, IrCl₃(tht)₃, can be prepared from IrCl₃·xH₂O in ca. 90% yield via a slight modification of the original synthesis.⁹ Reaction of IrCl₃(tht)₃ with allyllithium in benzene provides Ir(allyl)₃ in >90% NMR yield [eqn 1].¹⁰



Removal of the solvent *in vacuo* followed by hexane extraction, filtration, solvent removal and sublimation of the brown residue affords colorless, microcrystalline Ir(allyl)₃ in ca. 45% yield. Treatment of isolated Ir(allyl)₃ with PPh₃ in toluene gives the 1:1 adduct Ir(σ-allyl)(π-allyl)₂(PPh₃) **1** in high yield (Scheme 1).‡ Alternatively, the hexane filtrate from the synthesis of Ir(allyl)₃ can be used directly to prepare **1** with comparable efficiency. Although complex **1** did not react further with excess PPh₃, even at 100 °C, smaller phosphorus ligands such as PMe₃ and P(OPh)₃ yielded 1:2 adducts Ir(σ-allyl)₂(π-allyl)L₂ **2a,b**. The chelating bis(phosphine) 1,2-(PPh₂)₂C₆H₄ gave a similar product **3**. Addition of the tridentate phosphine PhP(CH₂CH₂PPh₂)₂ to Ir(allyl)₃ gave the tris(σ-allyl) complex **4**. Complexes **2–4** were prepared in >90% yield.

† Electronic supplementary information (ESI) available: preparative details and NMR data for **1–6** and crystallographic data for **1**, **3** and **4**. See <http://www.rsc.org/suppdata/cc/a9/a910164k/>



Scheme 1

The tris(allyl)iridium ligand adducts **1–4** were characterized by elemental analysis, NMR and IR spectroscopy, and, for **1**, **3** and **4** by single crystal X-ray diffraction (Fig. 1).§ IR analysis revealed that all phosphine adducts possess a characteristic C=C stretch in the region 1600–1610 cm⁻¹. ¹H and ¹³C NMR spectra of **1** confirmed the presence of one σ-allyl and two *inequivalent* π-allyl groups, even at 100 °C. The PPh₃ ligand is located *trans* to a methylene group of one of the π-allyl groups, as evidenced by the large P–C coupling constant (²J_{PC} 38 Hz). Room temperature spectroscopic characterization of complexes **2a,b** was also consistent with an unsymmetrical structure, but a dynamic process leads to equivalent phosphorus ligands and σ-allyl groups at 40 °C. The P–C coupling constants for **2a,b** (²J_{PC} 32.6, 47.5 Hz, respectively) indicate that the phosphines are *trans* to the methylenes of the π-allyl group and the σ-allyls are thus mutually *trans*. By contrast, complex **3** has inequivalent σ-allyl groups, 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 (Fig. 2). Adduct **4** has two sets of σ-allyl groups in a 1:2 ratio, consistent with C_s symmetry.

For compound **1**, the π-allyl ligand *trans* to P is symmetrically bound with typical Ir–C bond distances¹¹ (Ir–CH 2.143[5], Ir–CH₂ 2.201[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] cf. Ir–C(9) 2.196[4] Å}. A similar effect is seen in **3** {C(1)–Ir–C(7) 162.1(1)°; Ir–C(7) 2.270(2) cf. Ir–C(9) 2.202(3) Å}.

Reaction of Rh(allyl)₃¹² with PMe₃ afforded the 1:2 adduct **5** similar to **2a**. With triphenylphosphine¹² or better π-accepting ligands such as P(OPh)₃, however, only monovalent complexes, Rh(π-allyl)L₂ **6a,b** were obtained. Analogous complexes have been reported previously via alternative preparative routes.^{11,13} The reaction leading to **6b** was accompanied by formation of the C₆ hydrocarbons *n*-hexane, hex-1-ene and 2-methylpentane.¶

In summary, our improved preparation of tris(allyl)iridium has enabled us to demonstrate that, in contrast to its rhodium analog, addition of a range of phosphorus ligands gives stable trivalent adducts which show no tendency to undergo hydro-

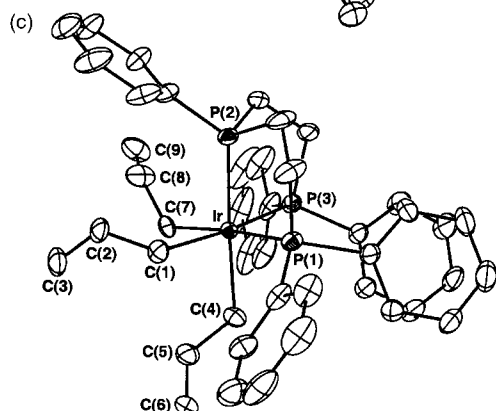
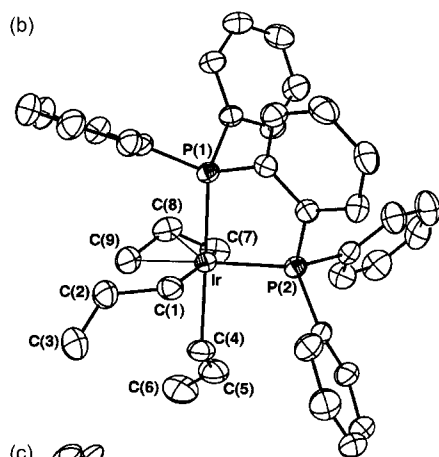
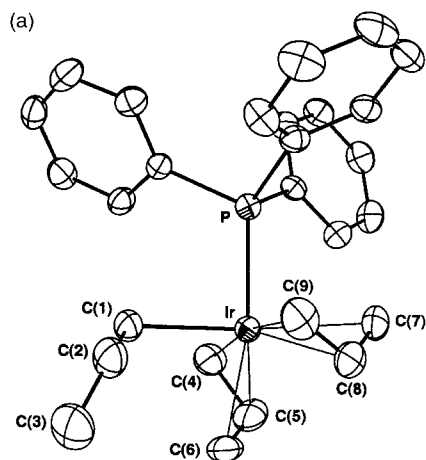


Fig. 1 Thermal ellipsoid representation of (a) **1**, (b) **3** and (c) **4** shown at the 50% probability level. For **1**, only one of the two molecules in the asymmetric unit is shown. For **1** and **4**, only one orientation of the disordered allyl group is shown. § Hydrogen atoms have been omitted for clarity.

carbon elimination reactions. We are currently extending these findings to prepare trivalent, ligated iridium moieties on metal oxide surfaces for use in hydrocarbon functionalization.

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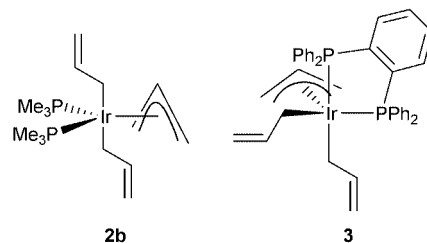


Fig. 2 Isomeric Ir(π -allyl)(σ -allyl) $_2$ L $_2$ structures.

paper is dedicated to Professor John P. Fackler, Jr. on the occasion of his 65th birthday.

Notes and references

‡ Preparation of Ir(σ -allyl)(π -allyl) $_2$ (PPh $_3$): to a room temperature solution of Ir(allyl) $_3$ (0.100 g, 0.32 mmol) in toluene (10 mL) 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 room temperature for 24 h to yield **1** as colorless crystals in 92.7% yield (0.170 g, 0.24 mmol). This procedure is representative of the syntheses of all of the phosphine complexes with the caveat that the preparation of **3** and **4** required brief heating (80 °C, 10 min) in order to dissolve the ligand.

§ CCDC 182/1552. See <http://www.rsc.org/suppdata/cc/a9/a910164k/> for crystallographic files in .cif format.

¶ Preparation of Rh(π -allyl)[P(OPh) $_3$] $_2$: to a room temperature solution of Rh(allyl) $_3$ (0.031 g, 0.14 mmol) in toluene (5 mL) 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 for an additional 2 h during which time the precipitate dissolved. The filtrate was then concentrated to ca. 2 mL and allowed to stand at -35 °C for 24 h to yield **2b** as yellow crystals in 96.7% yield (0.102 g, 0.13 mmol). GC-MS analysis of a portion of this reaction revealed that the organic products were *n*-hexane, 2-methylpentane and hex-1-ene.

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