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# *trans*-1,3-PENTADIENE AND CYCLOBUTENE COMPLEXES OF RHODIUM(I) AND IRIDIUM(I)

ROBERT B. OSBORNE and JAMES A. IBERS

*Department of Chemistry, Northwestern University, Evanston, Illinois 60201 (U.S.A.)*

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## Summary

The generation of "$MClL_2$" centers in THF solution ($M = Ir$, $L = AsPh_3$, $SbPh_3$; $M = Rh$, $L = SbPh_3$) leads to stable $\eta^2$-$MCl(C_5H_8)L_2$ complexes on the addition of an excess of *trans*-1,3-pentadiene. For $IrCl(PPh_3)_2$, it is only possible to recover a clean pentadiene complex if the reaction is carried out in neat diene solution.

Cyclobutene also coordinates to "$IrClL_2$" ($L = AsPh_3$, $SbPh_3$) to form an $IrCl(C_4H_6)L_2$ product when excess cyclobutene is condensed with a starting material at —78°C, THF is added, and the solution is warmed to 25°C.

These 16-electron $MCl(olefin)L_2$ complexes are stable to disproportionation after isolation from solution. The most stable complexes are formed with the tertiary arsine and stibine ligands for $M = Ir$.

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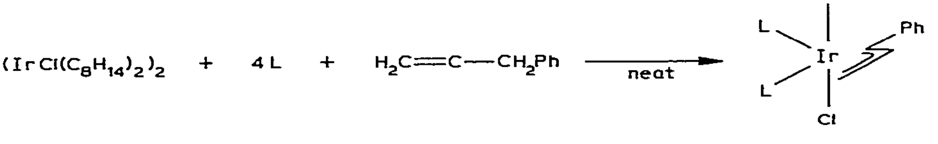
## Introduction

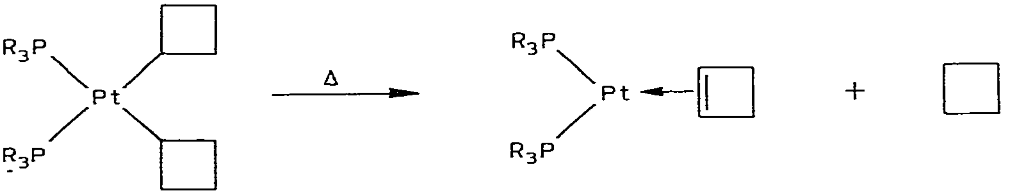
Complexes of rhodium(I) and iridium(I) are excellent hydrogenation and isomerization catalysts. Iridium(I) centers are especially proficient in the activation of C—H bonds for all types of olefins [1—3]. An unsaturated Ir center will abstract hydrogen from $sp^3$ C—H bonds in proximity to an open coordination site [4,5]. Thus, an allyl hydride has been isolated in the reaction with allylbenzene of the iridium(I) moiety "$IrClL_2$", generated in situ.



(1)

Tertiary Group V ligands L, such as $PPh_3$, $P(p\text{-tol})_3$, $AsPh_3$, $As(p\text{-tol})_3$, and $SbPh_3$, are effective; for the more basic phosphines, such as $PEt_3$, such an iridium(III) complex could not be isolated [6,7]. The object of the present study was to react such "$IrClL_2$" and "$RhClL_2$" moieties with other types of olefins bearing allylic protons, specifically *trans*-1,3-pentadiene and cyclobutene. *trans*-1,3-Pentadiene is the simplest conjugated diene with allylic protons. Cyclobutene possesses several allylic protons, but these protons are constrained to certain orientations by the geometry of the four-membered ring. These reactions provide some test of the generality of allylic C—H activation by metal(I) reagents.

$\pi$-Complexes of cyclobutene are more stable if there are electron-withdrawing substituents on the cyclobutene ring. Complexes of iron(0) with carboethoxycyclobutenes have been stabilized at low temperatures [8]. The most stable $\pi$-cyclobutene complexes are formed with $d^{10}$ platinum(0); perfluorocyclobutene [9], 1,2-dicyanocyclobutene [10], and 1-methyl-2-phenylcyclobutenedione [11] coordinate to Pt centers to form $Pt(olefin)(PPh_3)_2$ complexes. Unsubstituted cyclobutene has been complexed to platinum(0) by the degradation of dicyclobutylplatinum(II) complexes [12]:



(2)

The driving force for this type of reaction is the formation of cyclobutane, with the collapse of the fragments to form a platinum(0) complex. These cyclobutene complexes are labile, with R = Et more stable than R = Ph. The $PPh_3$ compound cannot be isolated cleanly [13].

## Experimental

### *General procedures and starting materials*

All reactions of rhodium(I) and iridium(I) organometallic systems were carried out under an atmosphere of pre-purified $N_2$. All solvents in the reactions were distilled under $N_2$. Proton NMR spectra were obtained with an 79.5 MHz Varian CFT-20 instrument with samples under $N_2$. Proton-decoupled $^{31}P\{^1H\}$ NMR spectra were obtained on a JEOL-FX-90Q variable probe instrument. Infrared spectra were recorded as Nujol mulls on a Perkin—Elmer 283 IR spectrometer.

*trans*-1,3-Pentadiene (99% purity) was purchased from the Aldrich Chemical Co. Cyclobutene was generated by an adaptation of the method of Roberts and Sauer [14].

The organometallic starting materials $(RhCl(C_2H_4)_2)_2$ [15] and $(IrCl(C_8H_{14})_2)_2$ [16] were prepared by previously published methods. Triphenylphosphine, triphenylarsine, and triphenylstibine were recrystallized before use.

Elemental analyses were performed by Micro-Tech Laboratories of Skokie, Ill. Owing to difficulties encountered in the purification of these materials the C analyses are generally low.

### *Synthetic procedures*

*Preparation of* $\mathit{IrCl(trans\text{-}CH_3CHCHCHCH_2)(AsPh_3)_2}$. The species "$IrCl(AsPh_3)_2$" was generated in solution by dissolving 46.1 mg $(IrCl(C_8H_{14})_2)_2$ (0.052 mmol) and 63.8 mg $AsPh_3$ (0.208 mmol) in 5 ml THF to yield an orange-red homogeneous solution. Next, 0.28 ml (2.8 mmol) of *trans*-1,3-pentadiene was syringed into this red solution; the color changed to a light yellow. After 18 h of stirring hexane was added to the solution to precipitate a 49% yield of a light yellow product. IR: $\nu(C{=}C)$ 1578, 1569 $cm^{-1}$. $^1H$ NMR $(C_6D_6)$: $\delta$ −0.28 (dd), 1.65 (d, 3H, $J$ 6.0 Hz), 1.81 (dd), 3.80 (ps-t), 5.20 (dd), 5.61 (dd). M.p. 135—140°C. Anal. Found: C, 54.54; H, 4.59; $C_{41}H_{38}As_2ClIr$ calcd.: C, 54.22; H, 4.22%.

*Preparation of* $\mathit{IrCl(trans\text{-}CH_3CHCHCHCH_2)(SbPh_3)_2}$. The analogous reaction with $SbPh_3$ was carried out by dissolving 45.2 mg $(IrCl(C_8H_{14})_2)_2$ (0.051 mmol) and 73.8 mg $SbPh_3$ (0.209 mol) in 5 ml THF to generate "$IrClSb_2$" as a dark red solution; 0.29 ml (2.9 mmol) of *trans*-1,3-pentadiene was syringed in to give an orange-yellow solution, which became a light yellow solution over time. After 18 h of stirring there was recovered by hexane precipitation a 39% yield of the iridium(I) $\pi$-complex, a pale yellow product. IR: $\nu(C{=}C)$ 1573, 1569 $cm^{-1}$. $^1H$ NMR $(C_6D_6)$: $\delta$ −0.19 (m), 1.45 (ps-q, $J$ 5.9 Hz), 1.79 (d, 3H, $J$ 5.6 Hz), 2.01 (m), 5.44 (d, $J$ 5.3 Hz), 5.35—5.51 (m). M.p. 166—170°C (dec.). Anal. Found: C, 48.19; H, 3.80; $C_{41}H_{38}ClIrSb_2$ calcd.: C, 49.15; H, 3.82%.

*Preparation of* $\mathit{RhCl(trans\text{-}CH_3CHCHCHCH_2)(SbPh_3)_2}$. To 19.5 mg $(RhCl(C_2H_4)_2)_2$ (0.050 mmol) was added 76.4 mg $SbPh_3$ (0.216 mmol) in 5 ml THF to generate a dark red solution. *trans*-1,3-Pentadiene (0.28 ml, 2.8 mmol) was syringed into the solution. The resultant orange-red solution was allowed to stir for 1.3 h. A 42% yield of desired product was recovered by hexane precipitation as a red-orange solid. IR: $\nu(C{=}C)$ 1571, 1567, 1558 $cm^{-1}$. $^1H$ NMR $(C_6D_6)$: $\delta$ −0.12 (bm), 1.58 (m), 1.72 (bd, 3H, $J$ 5.6 Hz), 5.05 (ps-t), 5.40 (t), 5.55 (t). M.p. 148°C (dec.). Anal. Found: C, 52.88; H, 4.03. $C_{41}H_{38}ClRhSb_2$ calcd.: C, 53.96; H, 4.20%.

*Preparation of* $\mathit{IrCl(trans\text{-}CH_3CHCHCHCH_2)(PPh_3)_2}$. A mixture of 44.8 mg $(IrCl(C_8H_{14})_2)_2$ (0.050 mmol) and 60.0 mg $PPh_3$ (0.229 mmol) was weighed into a flask. The solids were cooled to 0°C and 2.0 ml (20.0 mmol) of *trans*-1,3-pentadiene was syringed in under $N_2$. An orange solid was deposited, and after 15 min the orange suspension was warmed to room temperature. During 17 h of stirring, the orange solid was slowly taken up into solution and a colorless solid precipitated. The addition of hexane precipitated a 59% yield of the $\pi$-complex. IR: $\nu(C{=}C)$ 1586, 1571 $cm^{-1}$. $^1H$ NMR $(C_6D_6)$: $\delta$ −0.72 (m), 1.32 (m), 1.69 (td, 3H, $J_{HP}$ 6.6, $J_{HH}$ 1.1 Hz), 5.11 (m), 5.56 (m), 6.87 (m). $^{31}P\{^1H\}$ NMR ($C_6D_6$, 10°C) ($H_3PO_4$) AX pattern, dd, $\delta$ −9.1 and 3.9 ($J_{PP}$ 12.2 Hz). M.p. 139—142°C (dec.). Anal. Found: C, 58.70; H, 4.43. $C_{41}H_{38}ClIrP_2$ calcd.: C, 60.03; H, 4.67%.

*Preparation of* $\mathit{IrCl(\overline{HC{=}CHCH_2CH_2})(AsPh_3)_2}$. Cyclobutene (3.8 mmol) was transferred on a vacuum line into a flask with 93.4 mg $(IrCl(C_8H_{14})_2)_2$ (0.104 mmol) and 132.7 mg $AsPh_3$ (0.433 mmol) for an 18.4/1 molar excess of olefin per iridium(I) center. With the solids and cyclobutene at −78°C, 5 ml of THF was syringed in under $N_2$. The solution was slowly warmed to room temperature and stirred over a 7 h period. Hexane was added and the recovered solid was washed with 20 ml of hexane to give a 51% yield of the iridium(I)-cyclobutene complex. IR: $\nu$(C=C) 1580, 1560 cm$^{-1}$. $^1$H NMR ($CDCl_3$): $\delta$ 2.0—2.4 (low int. bm, 4H) 2.98, 3.02 (bs, 2H). M.p. 175—182°C (dec.). Anal. Found: C, 51.80; H, 3.99. $C_{40}H_{36}As_2ClIr$ calcd.: C, 53.23, H. 4.06%.

*Preparation of* $IrCl(H\overline{C{=}CHCH_2C}H_2)(SbPh_3)_2$. The analogous reaction of cyclobutene and "$IrClSb_2$" was carried out by condensing 4.3 mmol of cyclobutene with 92.7 mg $(IrCl(C_8H_{14})_2)_2$ (0.104 mmol) and 152.1 mg $SbPh_3$ (0.431 mmol) at —78°C; 5 ml THF was syringed in and the solution was warmed to room temperature over a period of 2 h. The product was precipitated with hexane to give a 48% yield. IR: $\nu$(C=C) 1572 cm$^{-1}$. $^1$H NMR ($CDCl_3$): $\delta$ 2.0—2.3 (low int. bm, 4H), 2.70 (bs, 2H). M.p. dec. above 220°C. Anal. Found: C, 49.15; H, 3.84. $C_{40}H_{36}ClIrSb_2$ calcd.: C, 48.63; H, 3.67%.

## Results and discussion

### *Diene coordination*

Reaction of *trans*-1,3-pentadiene with "$MClL_2$", M = Rh, Ir, affords the $\pi$-complexes (equations 3 and 4).

$$(IrCl(C_8H_{14})_2)_2 + 4L + \text{excess } trans\text{-}CH_3CHCHCHCH_2 \rightarrow trans\text{-}IrCl(C_5H_8)L_2 \quad (3)$$

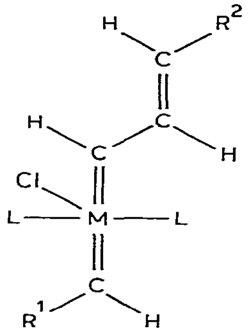
(L = $AsPh_3$, $SbPh_3$, ~25/1 excess diene, in THF; L = $PPh_3$, ~200/1 excess, neat diene)

$$(RhCl(C_2H_4)_2)_2 + 4L + \text{excess } trans\text{-}CH_3CHCHCHCH_2 \rightarrow trans\text{-}RhCl(C_5H_8)L_2 \quad (4)$$

(L = $SbPh_3$, ~25/1 excess in THF)

The "$MClL_2$" center is generated upon dissolution of a 4/1 tertiary ligand/metal—olefin dimer in a small volume of THF under $N_2$ [17]. Upon the addition of excess diene, coordination of the *trans*-1,3-pentadiene is rapid as judged by the color change. For the Ir complexes the dark red color of the unsaturated species is bleached rapidly to the pale yellow color of the four-coordinate complex. No change of color or reaction is observed on stirring these solutions overnight. The rhodium(I) solution also changes color on formation of the saturated 16-electron species, but the change is not as dramatic. The stable $MCl(C_5H_8)L_2$ complexes are light yellow (Ir) or orange-red (Rh) solids and are air stable when dried. In the region 1555—1580 cm$^{-1}$ of the infrared spectrum these complexes exhibit several $\nu$(C=C) bands arising from the bound pentadiene and the phenyl modes of the tertiary ligands. No other $\nu$(C=C) modes are observed down to 1480 cm$^{-1}$, at which point there are strong ligand absorptions.

The $^1$H NMR spectral pattern of the complexes provides some indication of the coordination pattern of diene to the metal. Vinylic protons undergo an upfield shift when a double bond is coordinated to a metal [17,18]. The $IrCl(C_4H_6)(PPh_3)_2$ complex [17], an $\eta^2$-butadiene compound of iridium(I), provides a good example of the proton chemical shifts of a diene bound by one of its double bonds. The "free" vinyl protons are at 5.56, 5.04, and 3.08 ppm, and the "bound" vinyl protons are shifted upfield to 0.90, —0.18, and —0.78 ppm, respectively. The $^1$H NMR spectra of the present pentadiene complexes are consistent with a preponderance of one of the two possible metal $\eta^2$-olefin isomers in each product.



(C(1)—C(2) binding :
$R^1$ = H , $R^2$ = $CH_3$ ;
C(3)—C(4) binding :
$R^1$ = $CH_3$ , $R^2$ = H )

In the $IrCl(C_5H_8)(SbPh_3)_2$ complex the diene appears to coordinate through the terminal C(1)—C(2) double bond to give the less crowded isomer. Three protons associated with C(1)—C(2) appear as multiplets at —0.19, 1.45, and 2.01 ppm, respectively. The $—CH_3$ doublet and two free olefin protons complete the spectrum.

The assignment of coordination mode in the other three complexes is not as straightforward. Coordination may be to the C(1)—C(2) bond or to the C(3)—C(4) internal double bond of the diene, based on the interpretation of free vs. bound vinyl proton positions; there is some indication that the internal double bond may be bound to the metal. The $IrCl(C_5H_8)(AsPh_3)_2$ complex has a set of three free vinyl protons (at 3.80, 5.20, and 5.61 ppm, respectively) with two bound vinyl protons and a $—CH_3$ doublet, consistent with coordination of the C(3)—C(4) internal double bond to the metal. The $IrCl(C_5H_8)(PPh_3)_2$ complex shows the same pattern, and the $CH_3$ protons are strongly coupled to the P nuclei into a triplet of doublets. The phosphines are non-equivalent, but there is apparently a near-equivalence of H—P coupling constants. The $RhCl(C_5H_8)(SbPh_3)_2$ complex shows three free vinyl protons, but the resonances are very broad.

Consistent with the known stereochemistry of the simple ethylene analogue, $IrCl(C_2H_4)(PPh_3)_2$ [17,19], we assume that the pentadiene complexes have the bound olefinic bond perpendicular to the coordination plane and that this bonding is relatively weak.

### *Cyclobutene reactions*

Cyclobutene will also coordinate to an "$IrClL_2$" center (eq. 5):

$$(IrCl(C_8H_{14})_2)_2 + 4\,L + \text{excess } \overline{HC{=}CHCH_2CH_2} \xrightarrow[THF]{} IrCl(\overline{HC{=}CHCH_2CH_2})L_2 \qquad (5)$$

(L = $AsPh_3$, $SbPh_3$)

The compounds were recovered by hexane precipitation and characterized by IR spectra, $^1H$ NMR spectra, and C/H elemental analyses.

These iridium—cyclobutene $\pi$-complexes are air stable. The C=C bands occur at 1580, 1560 (As), and 1572 $cm^{-1}$ (Sb); again there is an overlap of the olefin resonance with bands from the $AsPh_3$ and $SbPh_3$ ligands. The $^1H$ NMR spectral resonances of the two olefinic cyclobutene protons bound to the Ir center are shifted about 3 ppm upfield from 6.03 ppm in free cyclobutene [20]. These protons form a sharp unresolved peak. The four $CH_2$ ring protons are split into a broad low intensity region, shifted slightly upfield from 2.57 ppm in the free ligand [20]. These four protons are in approximately the same position and pattern as the unbound ring protons of the $Pt((NC)\overline{C{=}C(CN)CH_2C}H_2)(PPh_3)_2$ compound [10] *. Ring-opening of the cyclobutene is ruled out as a butadiene complex would have free and bound vinylic protons [17].

*Other reactions*

A number of reactions with other metal/ligand combinations and *trans*-1,3-pentadiene were attempted, but we were unable to isolate clean metal(I)—olefin or metal(III)—allyl hydride complexes. Thus, use of $PEt_3$, $PPh_3$, and $P(OPh)_3$ with iridium(I) or $PPh_3$, $P(OPh)_3$, and $AsPh_3$ with rhodium(I) were unsuccessful. Reactions of cyclobutene with L = $PPh_3$ for Ir and Rh were unsuccessful. Reactions of "$IrClL_2$" and "$RhClL_2$" with other olefins bearing allylic protons (vinylcyclopropane [21] and 1,4-pentadiene) were attempted, but no stable metal(I)—olefin or metal(III)—allyl hydride compounds were isolated. Some evidence of ring-opening of the vinylcyclopropane was seen, but no allylic abstraction of the doubly-activated C(3) protons of 1,4-pentadiene occurred in neat diene solution.

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* The four $CH_2$ ring protons of $Pt((NC)\overline{C{=}C(CN)CH_2C}H_2)(PPh_3)_2$ are split into a broad, low intensity region centered at $\delta$ 2.04 and 2.56 ppm.