Coordinatively Unsaturated Cationic Complexes of Rhodium(I), Iridium(I), Palladium(II), and Platinum(II). Generation, Synthetic Utility, and Some Catalytic Studies

Sir:

We have recently been investigating some cationic species of Rh(I) and Ir(I) which have interesting catalytic properties[1] and also form some unusual complexes.[2] In view of the catalytic and synthetic potential of such cations, we have sought a more general method for their production. We wish to report a procedure for the *in situ* generation of a wide variety of coordinatively unsaturated species,[3] [ML₂]⁺, from the readily accessible chloro-bridged dimeric complexes of the type [ML₂Cl]₂ (M = Rh, Ir, Pd, or Pt; L (or L₂) = ligand). These unique species are precursors to many new d⁸ cationic complexes such as π-arene compounds of Rh(I) and Ir(I), and to complexes which have previously been isolated by less general and/or less direct methods. We also report preliminary observations on the catalytic properties of these cationic species.[4]

The synthetic procedure is illustrated with the following example. [Rh(NBD)Cl]₂ (95 mg, 0.41 mmol; NBD = norbornadiene) in tetrahydrofuran[5] (*ca.* 2 ml) under an argon atmosphere is treated with AgPF₆ (104 mg, 0.41 mmol) dissolved in tetrahydrofuran (1 ml). Silver chloride is rapidly precipitated, and the solution is filtered under argon to yield 58 mg of AgCl (0.98 mol per mole of Rh) and a pale yellow filtrate. Conductivity, ¹H nmr, and ir studies of this and other such filtrates[6] indicate the presence of discrete monomeric ionic species of the type [Rh(NBD)]⁺PF₆⁻, whose solutions are reasonably stable, particularly under argon. Cationic species which may be generated by this method are collected in Chart I; their synthetic utility is illustrated in Chart II and Scheme I.

Solutions of **1a–d** and **2a**, when treated with donor ligands (*e.g.*, phosphines, arsines, phosphites, etc.), yield the corresponding four- or five-coordinate **8** in high yield. We have recently isolated a series of compounds **8** (M = Rh) by alternate routes and have described their utility as hydrogenation catalysts.[1] However, upon treatment of **1a–f** or **2** with benzene

(1) (a) J. R. Shapley, R. R. Schrock, and J. A. Osborn, *J. Amer. Chem. Soc.*, **91**, 2816 (1969); (b) R. R. Schrock and J. A. Osborn, *Chem. Commun.*, 567 (1970); (c) *J. Amer. Chem. Soc.*, **93**, 2397 (1971); (d) manuscript in preparation.

(2) R. R. Schrock and J. A. Osborn, *Inorg. Chem.*, **9**, 2339 (1970).

(3) The differentiation between a vacant and a solvent-occupied site is not always evident. Abstraction of chloride ion from the dimeric complexes yields species which are almost certainly not two-coordinate and strictly should be written [ML₂Sₙ]⁺, where n = 2 or 3. However, the chemical behavior of their solutions indicates that the solvent (S = THF or acetone) must be extremely labile, and "coordinatively unsaturated" is therefore perhaps the most appropriate, if not a rigorous, description. For this reason and for brevity, coordinated solvents are omitted in the formulas.

(4) Suitable elemental analyses have been obtained for all complexes described herein.

(5) Acetone or ethanol can also be used as solvents.

(6) (a) The conductivity of the filtrate in every reaction described herein was within 5% of that of an isolable, well-characterized, 1:1 ionic derivative in the same solvent.[1c] (b) An experiment performed with [Rh(NBD)Cl]₂ in acetone-d_6 gave a filtrate showing the presence only of coordinated norbornadiene at τ 5.98 (olefin, 4), 6.04 (methine, 2), and 8.82 (methylene, 2) (100 MHz, 35°, τ 5.98 and 6.04 peaks overlap). (c) No absorptions (*e.g.*, $\nu_{C=C}$) corresponding to free NBD could be found in the ir spectrum of [Rh(NBD)]⁺. More informative was the ir of the filtrate from a similar reaction employing [Rh(CO)₂Cl]₂ where two carbonyl stretching frequencies for [Rh(CO)₂]⁺ occurred at 2035 and 2112 cm⁻¹.

Chart I. The Generation of Coordinatively Unsaturated Cationic Species[a]

|	
[RhL₂]⁺ **1**	L₂ = norbornadiene (NBD, **1a**), 1,5-cyclooctadiene (COD, **1b**), 1,5-hexadiene (**1c**), 1,3-cyclohexadiene (**1d**); L = C₂H₄ (**1e**), P(OC₆H₅)₃ (**1f**), CO (**1g**)
[IrL₂]⁺ **2**	L₂ = COD (**2a**); L = cyclooctene (**2b**)
[M(enyl)]⁺	**3**, M = Pd; enyl = π-C₃H₅, π-crotyl, π-methallyl
	4, M = Pd; enyl = dicyclopentadiene-OCH₃, NBD-OCH₃, COD-OCH₃
	5, M = Pt; enyl = dicyclopentadiene-OCH₃

[a] See ref 3.

Scheme I. Derivatives of [ML₂]⁺; M = Rh(I) or Ir(I)
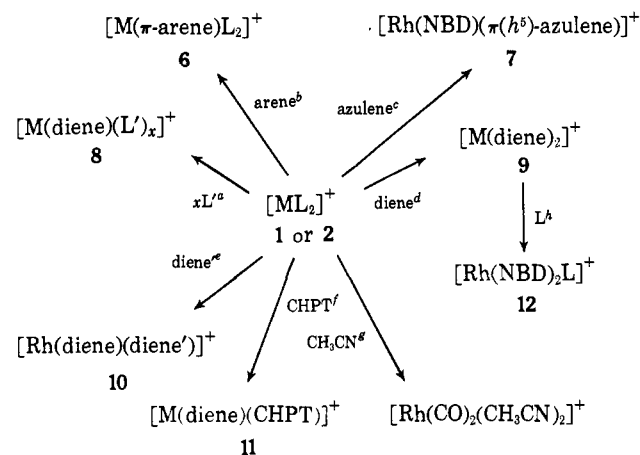
[a] See ref 1c, x = 2 or 3. [b] [ML₂]⁺ = **1a–f**, **2a**, or **2b**; arene = C₆H₆, 1,3,5-C₆H₃(CH₃)₃, or C₆(CH₃)₆. [c] M = Rh, L₂ = NBD. [d] M = Rh, diene (= L₂) = COD or NBD; M = Ir, diene (= L₂) = COD. [e] M = Rh, diene (= L₂) = NBD, diene' = COD. [f] CHPT = cycloheptatriene; M = Rh, diene (= L₂) = COD or NBD; M = Ir, diene (= L₂) = COD. [g] M = Rh, L = CO. [h] M = Rh, diene = NBD; L = CO, As(C₆H₅)₃, As(CH₃)₂C₆H₅, or Sb(C₆H₅)₃.

Chart II. Derivatives of Coordinatively Unsaturated Species of Pd(II) or Pt(II)
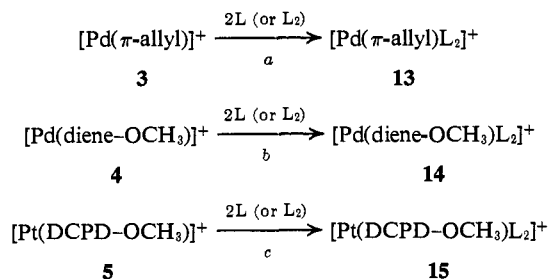
[a] Allyl = C₃H₅, crotyl, or methallyl; L = P(C₆H₅)₃, P(CH₃)₂C₆H₅, or As(CH₃)₂C₆H₅; L₂ = bipy, diphos, or COD. [b] diene = NBD or COD, L₂ = bipy, diene = dicyclopentadiene (DCPD), L₂ = bipy or COD. [c] L = P(C₆H₅)₃, L₂ = bipy, COD, or DCPD.

(or alkyl-substituted benzene), air-stable π-arene complexes, **6**, crystallize from solution. We have observed that complexes **6** are also produced in low yield by cyclic trimerization of acetylenes on the metal cation; *i.e.*, treatment of **1a** in acetone with an excess of 2-butyne at 25° gives a 15% yield of [Rh(NBD)(π-hexamethylbenzene)]⁺ after a few hours. The formulation of **6** was confirmed by elemental analyses, ¹H nmr, ir,

and conductivity data. These complexes are the only reported Rh(I) or Ir(I) π-arene complexes with the exception of [Rh(π-mesitylene)$_2$]$^+$.[7] The nmr spectra of **6** are temperature independent (-90 to $+40°$ in CH$_2$Cl$_2$), with the exception of [Rh(C$_2$H$_4$)$_2$(π-arene)]$^+$, where the temperature-dependent ethylenic resonances indicate ethylene rotation about the metal–olefin bond as found in the isoelectronic species Rh(π-C$_5$H$_5$)-(C$_2$H$_4$)$_2$.[8] The deep red azulene complex **7** can also be readily isolated, but in solution at room temperature ^{1}H nmr studies indicate the exchange between free and coordinated azulene to be rapid. At $-80°$, however, exchange is slow (vs. the nmr time scale at 100 MHz) and a structure with a $\pi(h^5)$ interaction between rhodium and the electron-rich five-membered ring is indicated.

Solutions of [M(diene)]$^+$ (**1a, 1b, 2a**)[9] react readily with several dienes to yield bright red to orange **9** or **10**, or with cycloheptatriene to yield yellow **11**. Complexes **9** were found to be active catalysts in hydrogenation and oligomerization reactions (vide infra). The stability of the five-coordinate adducts **12**, formed by addition of 1 mol of the ligand to **9**, is extremely sensitive to the choice of L, as discussed below.

The general reactions of **3** and **4** are collected in Chart II. Some of the complexes have been previously prepared,[10,11] often by less direct routes;[12] e.g., protonation of Pd(π-allyl)(acac) (acac = acetylacetonate) with HBF$_4$ followed by addition of L yields **13**. This route is not suitable for the preparation of **14** or **15**, since acidification results in loss of the methoxy group.[12] The silver ion method described here, however, provides a route to the previously inaccessible complexes **14** and **15**.

The utility of compounds **8** (M = Rh) as catalysts for hydrogenation of unsaturated substrates has been reported.[1] Of further interest is the ability of **8** (M = Rh) to reduce internal alkynes specifically ($>95\%$) to the corresponding cis-alkene in high yield ($>98\%$). Although the corresponding Ir(I) complexes (**8**, M = Ir) are less effective hydrogenation catalysts, [Ir(COD)$_2$]$^+$ (**9**) is very effective for the rapid reduction of 1,5-cyclooctadiene solely to cyclooctene.[13] However, the attempted catalytic hydrogenation of NBD with [Rh-(NBD)$_2$]$^+$ in acetone led to the uptake of only 0.4–0.5 mol of hydrogen per NBD double bond to yield ca. 80% of a species C$_{14}$H$_{18}$.[14] The structure and

mechanism of formation of this product, which is the result of a reductive dimerization of NBD, will be discussed fully elsewhere.[16]

The minor products in the reductive dimerization process described above result from the competitive catalytic dimerization of NBD. In the absence of hydrogen they are the sole products (two dimers and one trimer), identical, and produced in comparable ratios, with the products obtained upon refluxing NBD over a 5% rhodium-on-carbon catalyst.[15] Significantly, however, addition of 1 mol (per Rh) of L (L = P(C$_6$H$_5$)$_3$, P(C$_6$H$_5$)$_2$C$_6$H$_{11}$, or P(OC$_6$H$_5$)$_3$) to the catalyst solution results in the production of a third dimer, Binor-S,[17a] in 97% yield under identical conditions. Dimerization in absence of L clearly occurs via attack of NBD on the vacant coordination site of [Rh(NBD)$_2$]$^+$.[18] The stereochemistries of the former dimers are completely in accord with this mechanism. The blocking of the vacant site and the accompanying stereochemical change upon formation of [Rh(NBD)$_2$L]$^+$, however, directs intramolecular closure to Binor-S.[17b] This process is not dependent simply on stereochemical factors alone, since stable adducts **12** can be isolated which show negligible catalytic activity toward dimerization of NBD. Furthermore, the temperature-dependent ^{1}H nmr spectra of **12** show that rapid intramolecular rearrangement is occurring at ambient temperature.[19] Therefore, inaccessibility of a particular five-coordinate geometry is probably not significant to the catalytic process. Occupation of two sites on the metal (e.g., as in [Rh(NBD)(diphos)]$^+$) halts ready oligomerization activity toward NBD. Detailed discussions of these and related catalytic processes will be presented in due course.

(7) E. O. Fischer and H. H. Lindner, J. Organometal. Chem., 1, 307 (1964).

(8) R. Cramer, J. Amer. Chem. Soc., 86, 217 (1964).

(9) (a) During the course of this work, [Rh(NBD)$_2$]$^+$ and [Ir(COD)$_2$]$^+$ were independently isolated by a different route,[9b] but the catalytic and related properties reported here were not noted; (b) M. Green, T. A. Kuc, and S. H. Taylor, Chem. Commun., 1553 (1970).

(10) (a) J. Powell and B. L. Shaw, J. Chem. Soc. A, 774 (1968); (b) G. Paiaro and A. Musco, Tetrahedron Lett., 1583 (1965).

(11) (a) Belluco, et al.,[11b] have reported the isolation of **14** and **15** as chloride or bromide salts where diene–OCH$_3$ = DCPD–OCH$_3$ and L$_2$ = diphos, ethylenediamine, or bipy. Our attempts to prepare some of these salts employing a noncoordinating anion have not been successful; (b) P. Uguagliati, B. Crociani, and U. Belluco, J. Chem. Soc. A, 363 (1970).

(12) B. F. G. Johnson, J. Lewis, and D. A. White, J. Amer. Chem. Soc., 91, 5186 (1969).

(13) COD (1.0 ml) in 10 ml of acetone with 0.05 mmol of catalyst gave cyclooctene ($>98\%$ yield) at the rate of 0.2 mmol/min (30°, 1 atm total pressure). Less than 2% 1,3-COD was detected after the absorption of 1 mol of hydrogen, and subsequent reduction of cyclooctene was not observed.

(14) The molecular weight of C$_{14}$H$_{18}$ (**1**) was determined by mass spectroscopy. Substitution of H$_2$ by D$_2$ yielded C$_{14}$H$_{16}$D$_2$. **1** absorbed 0.98

mol of H$_2$ (5% Pd/C in ethanol), exhibited a multiplet at τ ca. 4 (area = 2), and showed a $\nu_{C=C}$ absorption at 1565 cm^{-1} (thin film). The hydrogenation of Katz's dimers[15a] (Pd/C) did not yield the hydrogenated product of **1**. **1** is possibly a species similar to Katz's dimer containing a norbornane (rather than a nortricyclene) system.

(15) (a) J. J. Mrowca and T. J. Katz, J. Amer. Chem. Soc., 88, 4012 (1966). (b) Dimers resulting from rearrangement of the carbon skeleton, as well as nonrearranged dimers, are obtained upon refluxing NBD with Rh(NBD)ClP(C$_6$H$_5$)$_3$: T. J. Katz, N. Acton, and I. C. Paul, ibid., 91, 206 (1969).

(16) Investigations so far show other dienes to undergo reduction to monoenes under similar conditions; e.g., 2,3-dimethyl-1,3-butadiene (1.0 ml) in 10 ml of acetone with 0.06 mmol of catalyst was reduced ($>95\%$) to a 3:2 mixture of tetramethylethylene and 2,3-dimethyl-1-butene, respectively, in 2 hr (30°, 1 atm total pressure).

(17) (a) G. N. Schrauzer, B. N. Bastian, and G. A. Fosselius, J. Amer. Chem. Soc., 88, 4890 (1966). (b) Examples of the catalytic production of Binor-S have been limited to heterometallic catalysts such as SnCl$_2$(Co(CO)$_2$)$_2$[17c] via a π-complex multicenter reaction.[17d] It must now be recognized, however, that dimerization to Binor-S can occur on mononuclear centers, binuclear catalysts not being uniquely active for its formation.[17e] Formation of Binor-S may be observed by nmr techniques in acetone-d$_6$ upon addition of 1 mol of P(C$_6$H$_5$)$_3$ to [Rh(NBD)$_2$]$^+$ or upon decomposition of the unstable five-coordinate adduct, [Rh(NBD)$_2$CO]$^+$. In both cases Binor-S was the only organic product observed. (c) F. P. Boer, J. H. Tsai, and J. J. Flynn, Jr., J. Amer. Chem. Soc., 92, 6092 (1970). (d) G. N. Schrauzer, Advan. Catal., 18, 373 (1968). (e) Note, for example, that use of a Lewis acid cocatalyst with Rh[P(C$_6$H$_5$)$_3$]$_3$Cl was found to promote Binor-S formation: G. N. Schrauzer, R. K. Y. Ho, and G. Schlesinger, Tetrahedron Lett., 543 (1970).

(18) [Rh(NBD)$_2$]$^+$ is stable in acetone for several days while ca. 10^3 mol of dimer is produced per mole of rhodium in the presence of NBD in 8–12 hr at 25°. NBD attack at the fifth coordination site is the major, if not the exclusive, pathway for production of Katz's dimers.

(19) Details of the mechanism of these rearrangements will be the subject of a forthcoming publication.

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A Versatile Synthesis of Cyclopentenones

Sir:

Δ^2-Cyclopentenones with vicinal disubstitution adjacent to the carbonyl function and away from the double bond (*e.g.*, I) are potentially versatile intermediates not only as such, but also because they can be

I   II
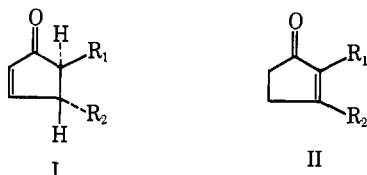
expected to equilibrate under a variety of circumstances to the (more stable) other α,β-unsaturated ketone (*e.g.*, II).[1]

We now report a synthesis of cyclopentenones of type I and their interconversion to II *via* the smooth thermal cracking of formal adducts of 1, *e.g.*, VIIb → VIIIb (*vide infra*).

The ketone III, readily available from dicyclopentadiene by oxidation with selenium dioxide followed by further oxidation of the allylic alcohol[2] (most efficiently with Jones' reagent), easily undergoes cuprous ion catalyzed addition of Grignard reagents. Addition of methylmagnesium halide thus leads to the expected V.[3] Initial attempts at interception of the intermediate enolate[4] IV with reactive halides (allyl bromide, methyl iodide) led, surprisingly, to mixtures containing appreciable amounts of α-dialkylated material. For in-

III   IV   V
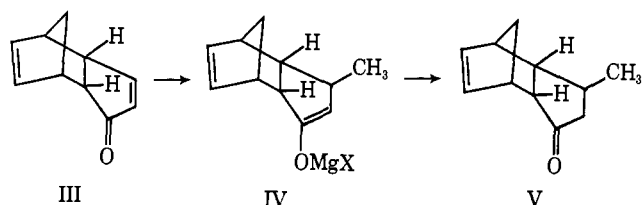
stance, replacement of the ether solvent after formation of IV by a 1:1 mixture of tetrahydrofuran–hexamethylphosphoramide and addition of 30% excess of methyl iodide, followed by 8–10 hr of stirring at room temperature and 5 hr of refluxing gave 90% yield of a mixture of 85% of the *trans*-dimethyl ketone VI (R = CH$_3$, R' = H) and 15% of the dimethyl derivative VI (R = R' = CH$_3$). Similarly, using allyl bromide as the alkylating agent, 50% of the VI (R = allyl, R' = H) and 20% of the diallylated compound (R = R' = allyl) were obtained. Not surprisingly, metallic

(1) For another synthesis of cyclopentenones of type I *cf.* D. P. Strike and H. Smith, *Tetrahedron Lett.*, 4393 (1970). These authors' interest in cyclopentenones of type I was related to their relationship to the prostaglandin system, a relationship which was also at the origin of the Columbia group's efforts described here.
(2) K. Alder and F. H. Flock, *Chem. Ber.*, 87, 1916 (1954); M. Rosenblum, *J. Amer. Chem. Soc.*, 79, 3180 (1957).
(3) T. Sakan and K. Abe, *Tetrahedron Lett.*, 2471 (1968).
(4) *Cf.* G. Stork, *Pure Appl. Chem.*, 17, 1383 (1968).

enolates, *e.g.*, lithium, sodium, which undergo more rapid proton transfer than magnesium enolates lead to even larger amounts of α-dialkylation. We have

VI
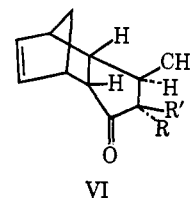
obtained evidence, based on the study of the alkylation of metalloenamines derived from V (*vide infra*), which allows a rationalization of the somewhat surprising ease with which dialkylation takes place; alkylation takes place largely (exclusively ?) from the exo side, in spite of the interference by the β-methyl group (leading to the kinetic formation of a cis α,β-disubstituted ketone), and the entrance of the second alkyl group is therefore not appreciably more hindered than that of the first.

Complete elimination of the troublesome dialkylation was achieved by using the metalloenamine procedure.[5] The crude cyclohexylimine from V and cyclohexylamine was transformed to the metalloenamine (1 equiv of lithium diisopropylamide—made *in situ* by addition of butyllithium to diisopropylamine in tetrahydrofuran—4.5 hr at room temperature) and the salt was treated with 1 equiv of *cis*-1-chloro-2-pentane[6] in tetrahydrofuran. After 14 hr at room temperature and 3-hr reflux, followed by hydrolysis of the imine (refluxing with sodium acetate–acetic acid–water (1:2:2) for 4 hr), the ketone mixture contained *only* the product VII of monoalkylation, in addition to some starting material. The α-alkylated product VIIa,b was obtained *in* 62% yield from V after chromatography on silica gel (elution with petroleum ether). Support for the contention above that entry of the alkyl group is from the exo side follows from the determination that the alkylated product thus obtained is a mixture of 53% VIIIa and 47% VIIb.[7]

Equilibration with 10% ethanolic potassium hydroxide (heating 1 hr) transformed the mixture into the essentially pure (>95%) trans isomer VIIb.

VIIa   VIIb
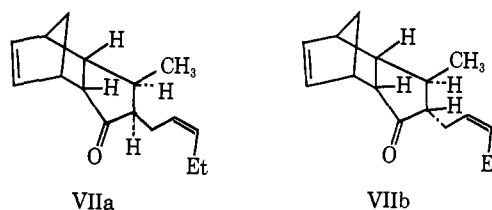
(5) G. Stork and S. Dowd, *J. Amer. Chem. Soc.*, 85, 2178 (1963).
(6) Kindly provided through the courtesy of Dr. W. I. Taylor, International Flavors and Fragrances, Union Beach, N. J.
(7) Determined by vpc analysis (Carbowax, 155°) after cracking to VIIIa, b; VIIIa has the shorter retention time. We believe that considerable equilibration takes place during the hydrolysis of the imine and that the kinetic product may well be exclusively cis. This view receives support from the observation that alkylation can become very difficult with ketones such as V in which groups much larger than methyl are present on the β carbon (observations by Dr. Gary Koppel in the Columbia Laboratories). The observation of exclusive trans products from the alkylation of enolates of V reflects, we believe, the much faster proton transfers with these enolates than with metalloenamines, transfers which are, of course, responsible for polyalkylation.