These results clearly indicate that energy transfer is at most a very minor part of the isomerization mechanism; note that the dideuterated case (*cis* → *trans*) would be expected to have an isotope effect of the order of 1.30 or so. Furthermore, comparison of quenching rates and triplet energies with dichloroethylene suggests that the expected rate of triplet energy transfer from benzophenone to 2-butene would be far less than the quenching rate observed. We therefore also feel that the observed isotope effect is not reasonably interpretable on the basis of competing Schenk and energy-transfer mechanisms.

A simple Schenk mechanism appears not to fit the experiments particularly well either, since the isotope effect is not inverse. Furthermore, we would expect the rate of *t*-butoxy radical additions to an olefin to be a reasonable ballpark guess as to the rate of reaction 5,[16] and that rate is probably several orders of magnitude lower than our quenching rate.[16,17]

It is our present hypothesis that the anomalously high quenching rate for 2-butene and other oxetane-forming olefins,[5,18] our isotope effect, and the observations that 1,4-biradical stability is often distinctly mediocre as a predictive device for the direction of oxetane formation from unsymmetrical olefins[3,19] all may be better interpreted on the basis of some intermediate prior to I. Further work on isotope effects and rates of oxetane formation should suggest whether electron-transfer complexes or exciplexes do in fact intervene.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research through Grant 3031-A4.

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(16) C. Walling and V. Kurkov, *J. Am. Chem. Soc.*, **88**, 4727 (1966), and references therein.

(17) Note that the only reported addition of *t*-butoxy radical to an unconjugated olefin is to the strained olefin norbornylene [E. Tobler, D. E. Battin, and D. J. Foster, *J. Org. Chem.*, **29**, 2834 (1964)], that abstraction of (unactivated) H-5 and H-6 is competitive, and that abstraction rates appear to be of the order of 10^3–10^4 M^{-1} sec^{-1}; see ref 16, D. J. Carlsson, J. A. Howard, and K. U. Ingold, *J. Am. Chem. Soc.*, **88**, 4725 (1966), and W. A. Pryor, "Free Radicals," McGraw-Hill Book Co., Inc., New York, N. Y., 1966, pp 75, 167.

(18) P. J. Wagner, private communication.

(19) S. G. Schroeter and C. M. Orlando, Jr., *J. Org. Chem.*, **34**, 1181 (1969).

(20) National Science Foundation Undergraduate Research Participant, Summer 1968.

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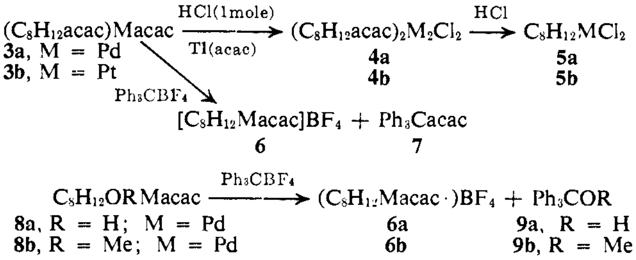
Cationic Transition Metal–Olefin Complexes

Sir:

Although many transition metal–olefin complexes are known, relatively few cationic derivatives have been reported.[1] This is possibly a reflection on the number of preparative methods at present available, and in general compounds of this type are prepared by the reaction of a suitable metal halide derivative in the presence of anhydrous aluminum trihalide and the appropriate olefin.[2] In connection with our studies of the reactivity of coordinated olefins,[3] we have examined the reaction of certain en-yl complexes of palladium(II) and platinum(II)[4] with electrophilic reagents such as triphenylmethyl tetrafluoroborate (**1**) and fluoroboric acid (**2**). These reactions led to the isolation of new cationic derivatives and suggested to us a convenient route to a variety of other cationic compounds of palladium(II), platinum(II), and rhodium(I).

Recently we reported the isolation and characterization of (acetylacetonato)(2-acetylacetonylcyclooct-5-en-yl)palladium(II) (**3a**), (Figure 1).[4] We have also shown previously that **3a** reacts with 1 mole of hydrochloric acid to produce di-μ-chloro-bis(2-acetylacetonylcyclooct-5-en-yl)palladium(II) (**4a**)[4] and with excess of that acid to generate (cycloocta-1,5-diene)dichloropalladium(II) (**5a**). We now wish to record that treatment of **3a** with triphenylmethyl tetrafluoroborate in methylene chloride, followed by the addition of ether, produces the yellow salt (acetylacetonato)(cycloocta-1,5-diene)palladium(II) tetrafluoroborate (**6a**) to which we assign the structure in Figure 2 on spectroscopic evidence (Table I) (see Scheme I). The other product from this reaction was identified as 3-triphenylmethylpentane-2,4-dione (**7**). This was initially assumed to arise by the attack of triphenylmethyl cation on the 2-acetylacetonylcyclooct-5-ene ligand, but the possibility that the initial attack by **1** occurred at the chelated acetylacetonato group followed by rearrangement cannot be ignored, and further attempts to determine the detailed mechanism operating in these reactions are currently in progress. Compound **6** was also obtained from the reaction of **1** with either (acetylacetonato)(2-methoxycyclooct-5-en-yl)palladium(II) (**8a**) or (acetylacetonato)(2-hydroxycyclooct-5-en-yl)palladium(II) (**8b**); in these reactions the organic products were methyl triphenylmethyl ether (**9a**) and triphenylmethanol (**9b**), respectively. The same cations have also been obtained by treatment of **3** or **8** with fluoroboric acid. By the above method a variety of cationic compounds of the general type [(β-diketonato)(diene)M$^{\text{II}}$]BF$_4$ (**10**) have been prepared.

Scheme I



$$(C_8H_{12}acac)Macac \xrightarrow[\text{Tl(acac)}]{\text{HCl(1mole)}} (C_8H_{12}acac)_2M_2Cl_2 \xrightarrow{\text{HCl}} C_8H_{12}MCl_2$$

3a, M = Pd; **3b**, M = Pt; **4a**, **4b**; **5a**, **5b**

$$(C_8H_{12}acac)Macac \xrightarrow{Ph_3CBF_4} [C_8H_{12}Macac]BF_4 + Ph_3Cacac$$

6; **7**

$$C_8H_{12}ORMacac \xrightarrow{Ph_3CBF_4} (C_8H_{12}Macac\cdot)BF_4 + Ph_3COR$$

8a, R = H; M = Pd; **8b**, R = Me; M = Pd; **6a**, **6b**; **9a**, R = H; **9b**, R = Me

In view of these results it appeared attractive to attempt the synthesis of other cationic derivatives by this method. The halogen-bridged dimers (**4**) react with cyclopentadienylthallium(I) to give unstable orange oils which rapidly decomposed on attempted purification. However, they are presumably the monomeric cyclopentadienyls (**11**) and on reaction with **1**, (cyclopentadienyl)(cycloocta-1,5-diene)palladium(II) (or -plat-

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(1) G. E. Coates, M. L. H. Green, and K. Wade in "The Transition Elements," Vol. 2, M. L. H. Green, Ed., Methuen and Co. Ltd., London, 1968.

(2) See, for example, E. O. Fischer and K. Ofele, Angew. Chem. Intern. Ed. Engl., **1**, 52 (1962).

(3) J. Lewis and A. W. Parkins, *J. Chem. Soc., A*, 953 (1969), and references therein.

(4) B. F. G. Johnson, J. Lewis, and M. S. Subramanian, *ibid.*, 1993 (1968).

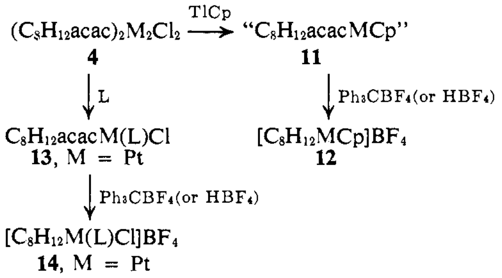
Table I. Spectroscopic and Conductivity Data

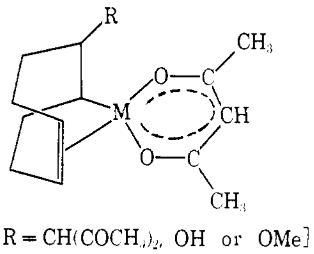
Compound	Ir spectrum, (ν_{CO}) cm^{-1} (Nujol)		Nmr spectrum (CDCl$_3$)[a] $\tau H^{(1)}$	$\tau H^{(2)}$	$\tau H^{(3)}$	$\tau H^{(4)}$	Λ_M[b] (acetone)
[C_8H_{12}Pd(acac)]BF_4	1522	1553	3.78 (4)	6.8–7.4 (8)	4.39 (1)	7.88 (6)	161
[C_8H_{12}Pt(acac)]BF_4	1533	1558	4.25 (4)	6.9–7.6 (8)	4.14 (1)	7.81 (6)	168
			J_{Pt-H} = 70 cps		J_{H-Pt} = 9 cps	J_{Pt-H} = 4.5 cps	

[a] With tetramethylsilane as internal standard; relative intensities shown in parentheses. [b] 10^{-3} *M* ohm^{-1} cm^2 mole^{-1}.

inum(II)) tetrafluoroborate (**12**) are obtained (Scheme II). The palladium cation has been reported previously.[5] Other mononuclear derivatives (**13**, M = Pt) were readily obtained from the dimer **4a** by reaction with tertiary phosphines or arsines (L); these also react with **1**, yielding the cationic complexes **14**. Attempts to prepare the palladium compounds (**13**, M = Pd) failed.

Scheme II



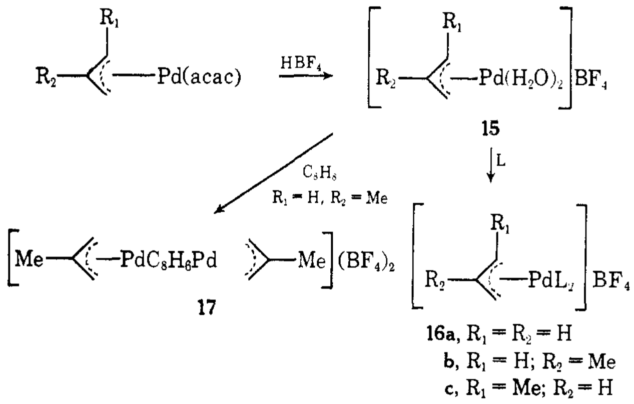


[R = CH(COCH$_3$)$_2$, OH or OMe]

Figure 1. Structure of C_8H_{12}RMacac.

We have also obtained cationic olefin complexes by the reactions outlined in Scheme III. In practice it is convenient, in these reactions, to generate the fluoroboric acid *in situ* by addition of wet ether to an equimolar mixture of the substrate and **1** in methylene chloride. Addition of cyclooctadiene to this mixture gives complexes such as **16a–c** (L_2 = C_8H_{12}). When cyclooctatetraene is used, a dimeric compound (**17**) has been isolated in which all four double bonds are coordinated to two metal atoms, as in μ-cyclooctatetraene-biscyclopentadienyldirhodium(I).[6] This preparative method is not limited to olefin complexes, and we have obtained a wide variety of compounds of type **16** in which L may be a tertiary phosphine, arsine, or stibine or L_2 a bidentate tertiary amine, phosphine, or arsine. Other substrates may also be used, thus **18** readily gives the compounds **19** (L = Ph_3P, Ph_2EtP, $PhEt_2P$, (p-MeC_6H_4)$_3$P, Ph_3As). With a similar range of ligands (L) compounds **21** have been prepared from the cyclooctadiene complex **20** (Scheme IV).

Scheme III



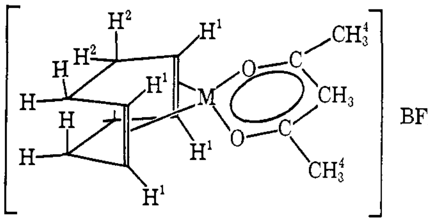
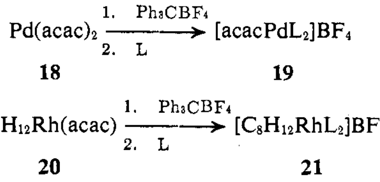


Figure 2. Probable structure of [C_8H_{12}Macac]BF_4.

Scheme IV



It is apparent that the methods described herein provide a general route for the preparation of a wide variety of cationic derivatives. Further work is in progress in these laboratories and fuller details will be published subsequently.

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