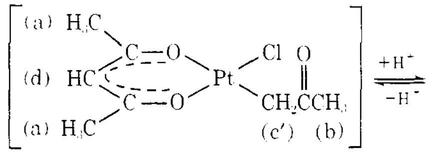
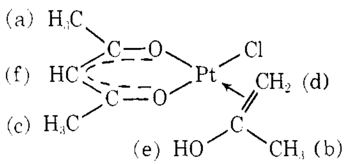
preparation of π-vinyl alcohol metal complexes may stimulate further interest in these complexes and the chemistry of vinyl alcohols.

Addition of aqueous KOH (0.2 ml of 0.663 *N*) to a THF solution of chloro(acetylacetonato)(ethylene)platinum(II) and excess acetaldehyde (31.03 mg and 2 ml, respectively, in 10 ml of solvent) at 0° results in effervescence and a deepening of the yellow color. After 30 min the solvent and excess acetaldehyde can be removed *in vacuo* at 0° and the residue recrystallized from warm absolute methanol with the addition of ether–hexane (1:1 by volume) to give a 55% yield (19.03 mg) of potassium chloro(acetylacetonato)(β-oxoethyl)platinate(II) (**1**) as greenish yellow crystals. As previously reported **1** can be readily converted to the π-ethenol, **2**, by protonation in aqueous solution; the two complexes existing in equilibrium in aqueous acetone as an acid and conjugate base.[6] The above products were identified by comparison of their ir spectra with those of authentic samples of **1** and **2**; within instrumental error, the spectra were identical.

The reaction conditions and the effervescence noted on the addition of aqueous KOH suggest that the reaction proceeds *via* carbanionic displacement of ethylene, rather than a possible oxidative mechanism, and is verified by the fact that under similar conditions acetone reacts with the ethylene complex to give the potassium chloro(acetylacetonato)(β-oxopropyl)platinate(II) complex, **3**, in 80–90% yields. One-half milliliter of 0.680 *N* KOH was added to 10 ml of acetone containing 100.6 mg of chloro(acetylacetonato)-(ethylene)platinum(II). After stirring at room temperature for 30 min the solution was evaporated to dryness under reduced pressure and the residue recrystallized from acetone and 1:1 ether–hexane to give 106 mg of **3** as bright yellow crystals, dec pt 158–172°. *Anal.* Calcd for $K[C_8H_{12}O_3PtCl]$: C, 22.6; H, 2.84; Pt, 45.8; Cl, 8.33. Found: C, 22.8; H, 2.68; Pt, 46.6; Cl, 9.46. The structure is confirmed by the intense ir absorption at 1645 cm^{-1} (C=O) and the nmr spectrum:[11] δ 2.42 (6 H_a, s), 2.75 (3 H_b, s), 3.94 (2 H_c, s), and 6.16 ppm (1 H_d, s). The ^{195}Pt–H coupling constants are <5, 18, 116, and 8 Hz, respectively. The value of 116 Hz for the two methylene protons is very near the value of 114 Hz observed for the β-oxoethyl complex.[6]



3



4

As in the case of the acetaldehyde complex, **3** can be converted to a vinyl alcohol complex by protonation. However, the sensitivity of the π-propen-2-ol complex, **4**, to water necessitates the use of anhydrous conditions. This was achieved by adding a slight excess of dry HCl, in the form a freshly prepared ether solution, to a suspension of the β-oxopropyl complex in ether. The resulting ether solution was reduced to small volume, dry hexane added until clouding had just initiated, and then cooled at −10°, yielding bright yellow crystals, dec pt 81–83° (yellow to orange), dec pt 165–185° (orange to black). *Anal.* Calcd for $C_8H_{13}O_3PtCl$: C, 24.8; H, 3.38; Pt, 50.7. Found: C, 24.42; H, 3.54; Pt, 51.5. The ir spectrum reveals a moderately intense band at 3230 cm^{-1} (OH) and the nmr spectrum[12] consists of six singlets at δ 1.88 (3 H_a), 2.02 (3 H_b), 2.03 (3 H_c), 3.96 (2 H_d), 5.03 (1 H_e), and 5.42 ppm (1 H_f). The ^{195}Pt–H coupling constants are ~6, 44, <5, 78, (undetected due to exchange broadening), and 8 Hz, respectively. The value of 78 Hz for the vinyl protons is quite reasonable when compared to the value of 71 and 76 Hz observed for the vinyl protons of **2**.[6]

The applicability of this new approach to vinyl alcohol complexes is currently being investigated for other transition metal systems. Attempts to obtain the ethenol and propen-2-ol complexes (**2** and **4**) *via* an acid catalyzed displacement of ethylene in acetaldehyde and acetone solutions have not been successful.

Acknowledgment. We wish to acknowledge the financial support of the R. A. Welch Foundation, Grant No. A-420.

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[11] Measured in D_2O *vs.* external TMS.

[12] Measured in $CDCl_3$ *vs.* internal TMS.

James Hillis, Minoru Tsutsui*
Department of Chemistry, Texas A&M University
College Station, Texas 77843

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Mechanistic Studies of Oxidative Addition to Low-Valent Metal Complexes. II. Reactions of α-Bromo Esters

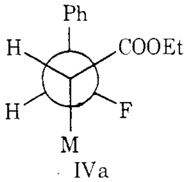
Sir:

We have recently reported evidence for a free-radical chain mechanism in the oxidative addition of several alkyl halides with Ir^I complexes, *e.g.*, *trans*-IrCl(CO)-$(PMe_3)_2$ (Ia).[1] In particular, these reactions show

$IrClCOL_2$
I

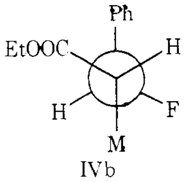
$IrClBr(CH_3CHCOOEt)COL_2$
III

a, L = PMe_3
b, L = PMe_2Ph
c, L = $PMePh_2$



IVa
Va

M = Br
M = $IrClBrCO(PMe_3)_2$



IVb
Vb

inhibition by radical scavengers, such as duroquinone and galvanoxyl, and are accompanied by loss of stereochemistry at the reacting α-carbon center. In contrast, the reaction of optically active $CH_3CHBrCOOC_2H_5$ (II) with *trans*-$IrCl(CO)(PMePh_2)_2$ (Ic) has been reported to proceed with substantial conservation of stereochemistry[2] suggesting that an alternative nonradical

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[1] J. S. Bradley, D. E. Connor, D. Dolphin, J. A. Labinger, and J. A. Osborn, *J. Amer. Chem. Soc.*, **94**, 4043 (1972).

mechanism may be occurring in the case of α-bromo esters. Since the stereochemical changes at carbon could not be unambiguously[3] determined using II, we have examined the reaction of a closely analogous substrate in which such changes can be monitored by nmr methods.

(*RS*,*SR*)-$C_6H_5CHFCHBrCOOC_2H_5$ (IVa) was prepared from *trans*-ethyl cinnamate by literature methods.[6] Reaction of IVa, in equimolar quantities with Ia in CH_2Cl_2 or acetone, was complete in seconds at ambient temperatures,[7] and a colorless solid could be isolated in *ca.* 60–80% yield and recrystallized from CH_2Cl_2–*n*-hexane. Nmr spectra (^1H, ^{19}F, ^{13}C) of the isolated adduct indicate it to be of configuration Vb.[8] However, the nmr spectra of the *reaction mixture before work-up* show the epimeric species Va also to be present in lower concentrations (Va:Vb 1:4.5).[9,10] Further, an identical product ratio of Va to Vb is afforded when Ia reacts with IVb,[11] clearly showing these reactions to take place with loss of stereochemistry at carbon. Moreover, formation of V is found to be retarded by small amounts of galvanoxyl, strongly indicating that these reactions also proceed *via* a free-radical mechanism.

Consequently we have examined the effect of galvanoxyl on the reaction of II with Ia and Ic; in both cases, pronounced inhibition was observed. Since the implications of this result appeared to be incompatible with the reported conservation of stereochemistry, we attempted to repeat the experiments with optically active II. Esterification of L-(+)-lactic acid followed by treatment with PBr_3[13] yielded optically pure D-(+)-II, with $[\alpha]_D$ +28.8° (CH_2Cl_2 solution).[14] Reaction with Ia–c in CH_2Cl_2[16] yielded the adducts IIIa–c, which were recrystallized from CH_2Cl_2–*n*-hexane and fully characterized by analysis and nmr. In all cases the optical rotation for both recrystallized and crude products was negligible ($[\alpha_D] \leq 0.2°$ (CH_2Cl_2)).[17] These results were reproducible over several experiments and under varying conditions (*e.g.*, care in degassing, purity of solvent and iridium complex). We considered the possibility that the observed racemization occurs subsequent to metal–carbon bond formation by dissociation of the proton from the α position, since the resulting carbanionic intermediate might be stabilized by the metal as well as the ester group. However, when Ic and II are allowed to react in CH_2Cl_2–CH_3OD, no deuterium is found in the adduct. Further, isolated Va is configurationally stable over long periods in solution alone or in presence of excess Ia.

We have examined the reactions of D-(+)-II with several other low-valent metal complexes. No reaction was observed with *trans*-$RhCl(CO)(PEt_3)_2$ under ambient conditions despite the fact that this complex reacts readily with CH_3I, and that for Ia the reactivities of CH_3I and II are comparable. Apparently a free radical pathway is less accessible for Rh(I) as compared with Ir(I). However, D-(+)-II reacts readily with $Pt(PPh_3)_2(C_2H_4)$ in benzene to yield a white solid characterized by elemental analysis, ir, and ^1H and ^{31}P nmr as $PtBr(CH(CH_3)COOC_2H_5)(PPh_3)_2$. The complex shows $[\alpha]_D$ −1.2°; the reaction is also inhibited by galvanoxyl. Again a mechanism predominately radical in nature is implied. Further, most (but not all) alkyl halide additions to $Pt(PEt_3)_3$ have been found to behave similarly, *e.g.*, *n*-butyl bromide addition is retarded by radical scavengers. Recently the addition of II to $Pd(RNC)_2$ was found to yield a racemic adduct.[18]

Hence, at least under the conditions of our experiments, addition of α-bromo esters to several low-valent transition metal complexes proceeds with loss of stereochemistry at carbon, *via* a free radical pathway. Kinetic studies have indicated that reactions of CH_3I and $C_6H_5CH_2X$ with *trans*-$IrCl(CO)(PPh_3)_2$ and $Pt(PPh_3)_3$ involve a nucleophilic-type mechanism.[19] Experiments with these halides in the presence of galvanoxyl show no inhibition, suggesting such a nonradical mechanism is indeed operative. However it is clear from these and other studies that radical routes in oxidative addition of C–X bonds are widespread. Further studies aimed at delineating the factors determining the choice of a particular mechanistic route are in progress.

Acknowledgments. Fellowships from the National Science Foundation (J. A. L.) and the Henry and Camille Dreyfus and Alfred P. Sloan Foundations (J. A. O) are gratefully acknowledged.

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(2) R. G. Pearson and W. R. Muir, *J. Amer. Chem. Soc.*, **92**, 5519 (1970).

(3) The conclusion that the reaction went with retention was based upon the belief that bromination of metal–carbon bonds proceeds with retention;[4] however, there are a number of examples of bromination in which inversion has been found.[5] Such an extrapolation is thus unwarranted.

(4) R. W. Johnson and R. G. Pearson, *Chem. Commun.*, 986 (1970).

(5) G. M. Whitesides and D. J. Boschetto, *J. Amer. Chem. Soc.*, **93**, 1529 (1971); F. R. Jensen, V. Madan, and D. H. Buchanan, *ibid.*, **93**, 5283 (1971); D. Dodd and M. D. Johnson, *Chem. Commun.*, 571 (1971).

(6) A. K. Bose, K. G. Das, and P. T. Funke, *J. Org. Chem.*, **29**, 1202 (1964).

(7) The reaction was followed by ir; carbonyl stretching absorbances for Ia (1945 cm^{-1}) and IVa (1740 cm^{-1}) disappear, while peaks due to V at 2040 cm^{-1} and 1705 cm^{-1} grow up.

(8) Inspection of Vb, assuming the predominant conformer is that shown, would predict large $^3J_{H-H}$ and $^3J_{C-F}$ values and a small $^3J_{H-F}$ value (observed data: 10.5, 20, and *ca.* 5 Hz, respectively). For Va the observed values are $^3J_{H-H} = 6.5$ and $^3J_{H-F} = 30$ Hz. Although these configurational assignments are entirely reasonable, it must be noted *rigorous* assignment is unnecessary in this case.

(9) Although Va and Vb are epimeric, they are *not* enantiomeric and have different ΔG values and physical properties, *e.g.*, solubility.

(10) Both the ^1H and ^{19}F nmr also show evidence for a side reaction, the extent of which depends markedly on experimental conditions. The ^1H spectrum indicates one product to be *trans*-ethyl cinnamate, resulting presumably from a β-fluoride elimination. The fluorine containing product has as yet not been characterized but is probably the FBr adduct of Ia. This side reaction does not result from decomposition of V.

(11) *cis*-Ethyl cinnamate was obtained by hydrogenating ethyl phenylpropiolate over $Rh(C_7H_8)(PMe_2Ph)_3^+$ as catalyst.[12] Treatment with *N*-bromoacetamide in HF gave a mixture of IVa and IVb which was enriched to about 50% IVb by careful distillation on a spinning band column. A pure sample of IVb could not be obtained.

(12) R. R. Schrock, Ph.D. Thesis, Harvard University, Cambridge, Mass., 1971.

(13) W. Gerrard and M. J. Richmond, *J. Chem. Soc.*, 853 (1945).

(14) $[\alpha]_D$ for the neat liquid was −31.9°, in good agreement with reported values.[13,15]

(15) J. W. Walker, *J. Chem. Soc.*, 914 (1895).

(16) Reactions were carried out in CH_2Cl_2 which had been distilled from CaH_2 and thoroughly degassed, with equimolar concentrations of reagents. The reactions were monitored by ir and required ∼30 sec, ∼30 min, and several days for complete reaction of II with Ia, Ib, and Ic, respectively.

(17) It has been reported[2] that starting with a sample of II with $[\alpha]_D$ −6° yields IIIc with $[\alpha]_D$ −20°; a similar degree of stereospecificity with our sample of II would have given IIIc with $[\alpha]_D$ +96°.

(18) S. Otsuka, A. Nakamura, T. Yoshida, M. Naruto, and K. Ataka, *J. Amer. Chem. Soc.*, **95**, 3180 (1973).

(19) P. B. Chock and J. Halpern, *J. Amer. Chem., Soc.*, **88**, 3511 (1966).

J. A. Labinger, A. V. Kramer, J. A. Osborn*
Department of Chemistry, Harvard University
Cambridge, Massachusetts 02138

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