in eq 9, $(3.55 \pm 0.07) \times 10^{-3}$ s^{-1}.

Experiments were done on the decomposition of the organocobaloxime in the presence of $Co(en)_3^{3+}$. In acidic solution it was without effect on the rates or product yields. This is to be expected since $Co(en)_3^{3+}$ does not react with $PhCHCH_3$ in acid, and its reaction with $Co(dmgH)_2OH_2$ is so slow that reaction 6 occurs instead. The concentration of Co^{2+} formed agreed exactly with $[PhCH(CH_3)Co(dmgH)_2OH_2]_0$.

In neutral solution, however, the rate constant when $Co(en)_3^{3+}$ was present was much smaller than k_b, and $[Co^{2+}]_\infty \approx (1.3–1.6) \times [PhCH(CH_3)Co(dmgH)_2OH_2]_0$. This suggests that the buildup of $Co(dmgH)_2OH_2$ suppresses at least partially the homolysis reaction, setting up a competition for the free radical. It may return to the starting complex by reaction with $Co(dmgH)_2OH_2$ or may be oxidized by $Co(en)_3^{3+}$. The effect is most pronounced when the reaction is run in the presence of added $Co(dmgH)_2OH_2$.

The relative yields of styrene are 1:22:7 in the following three experiments involving decomposition of (α-phenylethyl)aquocobaloxime (a) in the presence of $Co(en)_3^{3+}$ in neutral solution, (b) alone in neutral solution over a longer period of time, and (c) with $Co(en)_3^{3+}$ in acidic solution. The much diminished yield of styrene in the first experiment is consistent with oxidation of the radical by $Co(en)_3^{3+}$ under these conditions. Only in c is a substantial quantity of dimers A–D produced; styrene is the only appreciable organic product of b.

Conclusions. The data obtained in this study support the occurrence of parallel homolysis and β-elimination pathways for decomposition of $PhCH(CH_3)Co(dmgH)_2OH_2$. The former is readily reversed, such that when $[Co(dmgH)_2OH_2]$ is allowed to accumulate as in neutral solution, the reaction occurs largely by β elimination. This appears to have been the situation in Gaudemer's work,[4] and the conclusion that decomposition occurs only by β elimination is the correct one *for the conditions employed.* On the other hand, homolytic Co–C cleavage becomes the major pathway under conditions in which a reagent which reacts rapidly with $Co(dmgH)_2OH_2$ is present. In that case the inorganic and organic products can be quantitatively attributed to these intermediates.

The question remains which is the predominant pathway in toluene.[5] Since $Co(dmgH)_2py$ is stable under those conditions, it seems likely that the contribution of homolysis is suppressed and that the major pathway is β elimination. The small values of ΔS^* under those conditions[5] as compared to that when homolysis can be authenticated (1.4 vs. 25.7 cal mol^{-1} K^{-1}) lends support to that argument.

Acknowledgment. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division, under Contract No. W-7405-ENG-82.

Registry No. A, 4613-11-0; B, 2726-21-8; C, 80326-00-7; D, 1520-44-1; styrene, 100-42-5; $PhCH(CH_3)Co(dmgH)_2(H_2O)$, 14783-95-0; $PhCH(CH_3)Co(dmgH)_2(py)$, 37824-58-1; $RCo(dmgH)_2OH_2$ (R = 2-propyl), 28132-41-4; $RCo(dmgH)_2OH_2$ (R = ethyl), 10210-55-6; Co^{2+}, 22541-53-3; $(H_2O)_2Co(dmgH)_2^+$, 46932-87-0; $HCo(dmgH)_2OH_2$, 80327-77-1; $Co(dmgH)_2OH_2$, 80327-78-2; $BrCo(dmgH)_2OH_2$, 51446-51-6.

Disproportionation of Monoorganothallium(III) Compounds Induced by Trimethyl Phosphite and Related Reagents: Evidence against a Spontaneous Disproportionation Mechanism

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The mechanism of the reaction between organothallium(III) diacetates ($RTl(OAc)_2$) and trimethyl phosphite, which gives R_2TlOAc as the main product, was reexamined primarily on the basis of stereochemical and kinetic considerations. The reaction is suggested to proceed through an initial $RTl(OAc)_2$–$P(OMe)_3$ interaction rather than via spontaneous disproportionation of $RTl(OAc)_2$ into R_2TlOAc and $Tl(OAc)_3$ as originally proposed, enhancing the reactivity of the compounds with respect to R_2TlOAc formation. The implications of such disproportionation as a potential obstacle in the synthetic application of $RTlX_2$ are pointed out.

Redistribution of organic groups (disproportionation hereafter) of organometallic salts has received much attention, particularly in recent years, from an environmental chemical point of view.[1,2] The disproportionation of RHgX is believed[3] to proceed through the complexation of Lewis bases with either RHgX or HgX_2 formed in a preequilibrium and the electron transfer from reductants to RHgX. Recent studies[2,4] related to the biomethylation of Tl^I suggested that disproportionation of $RTl(OAc)_2$ (R = Me, Ph) with $P(OMe)_3$ (eq 1)[5] proceeds through initial

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(2) Huber, F.; Schmidt, U.; Kirchmann, H. "Organometals and Organometalloids. Occurrence and Fate in the Environment"; Brinckman, F. E., Bellama, J. M., Eds.; American Chemical Society: Washington, D.C. *ACS Symp. Ser.* **1978**, p 65.

(3) Jensen, F. R.; Rickborn, B. "Electrophilic Substitution of Organomercurials"; McGraw-Hill: New York, 1968; p 120.

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(5) This reaction is also useful for the synthesis of a variety of diarylthallium(III) compounds from readily accessible arylthallium(III) bis(trifluoroacetates).[6]

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$$2\underset{\textbf{1a–e}}{RTl(OAc)_2} + P(OMe)_3 \xrightarrow{MeOH} \underset{\textbf{2a–e}}{R_2TlOAc} + TlOAc + OP(OMe)_3 + MeOAc + HOAc \quad (1)$$

a, R = PhCH(OMe)CH_2; **b**, R = Me; **c**, R = PhCH=CH; **d**, R = *p*-MeC_6H_4; **e**, R = Ph

$$2\underset{\textbf{1}}{RTl(OAc)_2} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \underset{\textbf{2}}{R_2TlOAc} + Tl(OAc)_3 \quad (2)$$

spontaneous disproportionation (eq 2), followed by rapid reduction of $Tl(OAc)_3$ by $P(OMe)_3$. However, no spectral evidence was found to support the occurrence of such spontaneous disproportionation. Our recent finding[7] that radical intermediates participate in the reductant-induced disproportionation of alkylthallium(III) compounds prompted us to examine the mechanism of eq 1 in more detail. We report evidence to suggest the occurrence of a direct $RTl(OAc)_2$–$P(OMe)_3$ interaction which leads to R_2TlOAc. We further emphasize implications of this type of disproportionation as a potential obstacle in synthetic applications of $RTlX_2$ compounds.

Results and Discussion

Disproportionation of $RTl(OAc)_2$ with $P(OMe)_3$. The stereochemistry of the reaction of alkyl analogues with $P(OMe)_3$ was examined by employing the stereoisomer *erythro*-PhCH(OMe)CHDTl(OAc)$_2$ (*erythro*-**1a**-*d*) obtainable from the trans oxythallation of (*E*)-PhCH=CHD.[8] The main product from the reaction of **1a** with $P(OMe)_3$ in THF/MeOD was **2a** (84%), with small amounts of styrene and α-(methoxyethyl)benzene also being obtained. The ^1H NMR spectrum of the deuterium analogue of **2a** obtained from *erythro*-**1a**-*d* showed that 70% of the total alkyl groups had undergone epimerization. This degree of stereochemical loss is similar to that found during the disproportionation of *erythro*-**1a**-*d* with hydrazine and ascorbic acid,[7] as well as that in the electrochemical generation of **2a**-*d* from *erythro*-**1a**-*d*.[9] *erythro*-**1a**-*d* is stereochemically stable unless treated with reducing agents. Further, the erythro/threo ratio in the sample of **2a**-*d* obtained above no longer changed when this material was allowed to be in contact with an excess of $P(OMe)_3$.

Next we examined the stereochemistry of the reaction of the vinyl analogues. The *E* isomer of **1c** reacted with $P(OMe)_3$ in CD_3OD[10] to give the *E*,*E* isomer of **2c** and (*E*)-PhCH=CHD in comparable yields, showing retention of stereochemistry. The formation of styrene in this case consumed $P(OMe)_3$ according to eq 3. Although we could

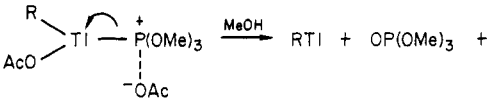
$$RTl(OAc)_2 + P(OMe)_3 \xrightarrow{MeOH} RH + TlOAc + OP(OMe)_3 + MeOAc \quad (3)$$

not obtain the pure *Z* analogue of **1c**, we treated a *Z*/*E* mixture (*Z*/*E* = 70/30) of **1c** with $P(OMe)_3$ in CD_3OD and found retention of this *Z*/*E* ratio in the products PhCH=CHD (56%, *Z*/*E* = 76/24) and **2c** (44%, *Z*/*E* = 63/37). In the latter product only the overall *Z*/*E* ratio could be determined by ^1H NMR spectroscopy of the reaction mixture. The somewhat smaller *Z*/*E* ratio in **2c** than in **1c** suggests a greater reluctance of the (*Z*)-PhCH=CH group to undergo disproportionation, possibly owing to the greater steric congestion in the transition state involving Tl···vinyl···Tl bridging.

Huber and co-workers suggested that the forward path of eq 2 is rate determining in eq 1.[2,4] However, we could not detect any formation of **2** in the ^1H NMR spectrum of **1** (concentration range 0.1–0.2 mol/L) in CD_3OD. The lowest limit of detection in the spectroscopy suggests that the equilibrium concentrations of **2** and $Tl(OAc)_3$, if any, should be at most 1/20 of that of **1**. It follows that the equilibrium constant, k_1/k_2, is smaller than 1/400.

We next tried to estimate the order of k_2. **2a** and **2b** did not react at all with $Tl(OAc)_3$ under conditions similar to those used in eq 1, even after a long period (>2 days). This observation together with $k_1 < k_2/400$ leads to the unlikelihood of the forward path of eq 2 being rate determining in the very fast reaction of eq 1 (R = PhCH(OMe)CH_2, Me; almost complete within 1 h). The reaction of (*E*,*E*)-**2c** with $Tl(OAc)_3$ was indeed fast (complete in 10 min), while **2d** reacted with $Tl(OAc)_3$ at such a rate that could allow us to follow the reaction by ^1H NMR spectroscopy. Thus, we observed that at $[\mathbf{2d}]_0 = [Tl(OAc)_3]_0 = 0.07$ mol/L and 26 °C in CD_3OD, the first half-life is approximately 3 min and the time required for 80% completion is ca. 10 min. This leads to the prediction that the first half-life of the forward path of eq 2 (R = *p*-MeC_6H_4), if $[\mathbf{1d}]_0 = 0.14$ mol/L, is more than 1200 min and the time required for 80% completion is more than 4000 min. In fact, however, the reaction between **1d** and $P(OMe)_3$ in CD_3OD with the corresponding order of concentrations and temperatures was completed in much less than half an hour, affording a ca. 1:1 mixture of **2d** and toluene.

It is now reasonable to assume other disproportionation mechanism(s) than the one involving eq 2. Presumably, the initial step common in eq. 1 is the coordination of $P(OMe)_3$ to thallium. The complex $PhTlCl_2 \cdot PPh_3$ was reported to give, when heated in methanol, benzene, TlCl, and $OPPh_3$ almost quantitatively.[11] Such complexation of PR_3 may both increase the electron density on thallium and promote reduction of Tl^{III} (e.g., eq 4), making the



MeOAc + HOAc (4)

thallium-bound carbon more susceptible to electrophilic attack (stereospecific in the case of the sp^2 carbon) by protons or another thallium atom. However, it is difficult to determine explicitly at which stage (before, simultaneously with, or after the reduction of Tl^{III}) such electrophilic attack takes place. As for the protolysis, we assume the first case (before the reduction) is unlikely, since even $R_2TlX \cdot L$ compounds, which are expected to be more easily cleaved by the electrophiles than $RTlX_2 \cdot L$ compounds, are stable to protolysis. The ease with which the protolysis of monoaryl- and monovinylthallium(III) compounds is accomplished by the action of $NaBH_4$[12] may be explained similarly by the occurrence of ready redox processes such as eq 5.

In the case of the disproportionation of the alkylthallium(III) analogues with $P(OMe)_3$, electron-transfer

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(9) Nogami, J.; Okawara, R., private communication.
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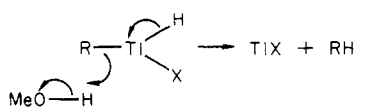
(12) Uemura, S.; Tara, H.; Okano, M.; Ichikawa, K. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 2663. Herbert, R. B. *Tetrahedron Lett.* **1973**, 1375.



(5)

may precede, at least in part, the intermolecular alkyl transfer in view of the stereochemical results employing *erythro*-**1a**-*d*. One-electron transfer to $RTlX_2$ and RHgX which induces radical generation and subsequent formation of the disproportionation products containing the racemized or epimerized alkyl group is already known.[3,7]

Disproportionation of $RTlX_2$ with a Potential Electron Donor in A Synthetic Application. One of the most useful reaction patterns of organothallium compounds for organic synthesis is shown in eq 6.[13] However,

$$RTlX_2 + Y^- \rightarrow RY + TlX + X^- \quad (6)$$

since the nucleophile to be used in eq 6 could be a potential electron-donor or reducing agent, there might be a chance that the formation of R_2TlX competes with or dominates over the formation of RY. Indeed we have found the undesirable formation of a diphenylthallium(III) species in high yield in attempts to substitute the $CH(COMe)_2$ group[14] for the $Tl(OAc)_2$ moiety of **1e**. The reaction of **1e** with NaSPh similarly gave the diphenylthallium(III) compounds. These disproportionations also may have been induced by the coordination of **1e** with the nucleophile, since the diphenylthallium(III) compounds were found to form much more rapidly than expected from the hypothetical spontaneous disproportionation of **1e**.

In similar attempts by us and by others to replace the $Tl(OAc)_2$ moiety of **1a** by SPh (with NaSPh), hydrido (with $NaBH_4$),[16] and halogen (with CuX/KX, X = Cl, Br)[17] groups, substantial yields (up to 40%) of dialkylthallium(III) species were formed, together with varying yields of the intended products. Notably, the reaction with CuX/KX was demonstrated to involve the alkyl radical intermediate in the main course,[17] and the dialkylthallium(III) product from *erythro*-**1a**-*d* and $NaBH_4$ contained the partially epimerized alkyl group.[7] Furthermore, *erythro*-**1a**-*d* and NaSPh gave PhCH(OMe)CHDSPh with complete epimerization, although the stereochemistry of the disproportionation product (supposedly $[PhCH(OMe)CHD]_2TlSPh$) could not be determined owing to its poor solubility. It may well be that the formation of the dialkylthallium(III) compounds in the three reactions above is again induced by electron transfer to **1a** followed by Tl–C bond homolysis.

Not all of the reactions of $RTlX_2$ which proceed through the electron transfer from reductants to $RTlX_2$ afforded the disproportionation products. Typical examples without disproportionation include hydrodethallation[18] and carbodethallation[19] of **1a** with 1,4-dihydronicotinamide and $Me_2CNO_2^-$, respectively. In order to make the synthetic application of $RTlX_2$ more general, one needs to know more about the factors affecting the choice between the formation of R_2TlX and the substitution products.

Experimental Section

Materials. (*E*)-**1c** was prepared by the reaction of (*E*)-PhCH=CHB(OH)$_2$ with $Tl(OAc)_3$ (1:1) in methanol and recrystallized from methanol–diethyl ether: mp 155 °C dec; ^{1}H NMR (CD_3OD) δ 7.03 (d, J_H = 16.0, $J_{^{205}Tl}$ = 1580 Hz, CH^1=), 7.15 (d, $J_{^{205}Tl}$ = 1555 Hz, CH^2=). Anal. Calcd for $C_{12}H_{13}O_4Tl$: C, 33.87; H, 3.08. Found: C, 33.81; H, 3.22. The reaction of $B(OMe)_3$ with the Grignard reagent prepared from pure (*Z*)-PhCH=CHBr gave only a *Z*/*E* mixture of PhCH=CHB(OH)$_2$, which was used in the reaction with $Tl(OAc)_3$ without further purification. (*Z*)-**1c**; ^{1}H NMR (CD_3OD) δ 6.35 (d, J_H = 9.0, $J_{^{205}Tl}$ = 1495 Hz, TlCH=), 7.51 (d, $J_{^{205}Tl}$ = 3490 Hz, PhCH=). An authentic sample of (*E*,*E*)-**2c** was prepared from the boronic acid and $Tl(OAc)_3$ (2:1): mp 235 °C dec; ^{1}H NMR (CD_3OD) δ 7.12 (br, J_{Tl} = 715 Hz, C*H*=C*H* overlapping). Anal. Calcd for $C_{18}H_{17}O_2Tl$: C, 46.03; H, 3.65. Found: C, 46.21; H, 3.72. The *Z*/*E* mixture of **2c** was prepared similarly. (*Z*)-**2c**: ^{1}H NMR (CD_3OD) δ 6.70 (d, J_H = 10.5, $J_{^{205}Tl}$ = 385 Hz, TlCH=), 7.93 (d, $J_{^{205}Tl}$ = 1520 Hz, PhCH=). The *p*-tolyl compound **1d** and **2d** were prepared similarly. **1d**: mp 206 °C dec. Anal. Calcd for $C_{11}H_{13}O_4Tl$: C, 31.95; H, 3.17. Found: C, 32.07; H, 3.29. **2d**: mp above 250 °C. Anal. Calcd for $C_{16}H_{13}O_2Tl$: C, 43.12; H, 3.84. Found: C, 42.92; H, 3.96. For ^{1}H NMR identification of **1d** and **2d**, see ref 6. An authentic sample of **2a** was prepared by the reaction of **1a**[17] (1.2 mmol) with hydrazine hydrate (3.5 mmol) in methanol (8 mL) under nitrogen at room temperature for 3 h. After the solvent was evaporated under vacuum, the residue was extracted with chloroform (10 mL × 2). The chloroform solution was concentrated to give white solids which were recrystallized from chloroform–hexane to give white crystals of **2a** (60%): mp 113–114 °C dec; ^{1}H NMR ($CDCl_3$) δ 2.15 (br, J_{Tl} = 370 Hz, $TlCH^1H^2$), 2.33 (br, J_{Tl} = 490 Hz, $TlCH^1H^2$; for the assignment of H^1 and H^2, see ref 8), 4.75 (br, J_{Tl} = 420 Hz, CH<). Anal. Calcd for $C_{20}H_{25}O_4Tl$: C, 45.00; H, 4.72. Found: C, 45.02; H, 4.70.

Reaction of 1 with $P(OMe)_3$. The reaction of **1a** (1 mmol) with $P(OMe)_3$ (1 mmol) was carried out in an oxygen-free THF (10 mL)–CH_3OD (2 mL) mixture at room temperature. GLC analysis (PEG-1000, 3 mm × 1 m) after 1 h confirmed the formation of styrene (6%) and α-(methoxyethyl)benzene (7%). The solvents were removed under vacuum. To the residue was added $CDCl_3$ containing a known amount of toluene as internal reference, and the $CDCl_3$ solution was examined by ^{1}H NMR spectroscopy. The erythro/threo ratio in **2a**-*d* was determined by the relative area of the methylene proton peaks (H^1 and H^2) that were corrected for small amounts (~10%) of **1a** and *threo*-**1a**-*d*, which contaminated the *erythro*-**1a**-*d* used. The reaction of **1c** and **1d** with $P(OMe)_3$ was carried out in CD_3OD at room temperature by employing the concentration range of 1 and $P(OMe)_3$ (1:1) appropriate for ^{1}H NMR analyses (0.1–0.5 mol/L).

Reaction of 1 with Other Reagents. Addition of NaSPh (2 mmol) in methanol (10 mL) to **1e** (1 mmol) in the same solvent (10 mL) gradually gave a pale yellow precipitate. GLC (SE-30, 3 mm × 1 m) and ^{1}H NMR analyses of the filtrate showed the formation of benzene (85%) and diphenyl disulfide (87%). ^{1}H NMR spectra ($(CD_3)_2SO$) of the precipitate showed the presence of the diphenylthallium(III) species (no acetate ion present, possibly the thiophenoxide) in 11% yield. The reaction of **1a** with NaSPh (1:2) was carried out similarly. ^{1}H NMR spectra ($CDCl_3$) of the yellow precipitate which was formed showed very broad, weak absorptions quite similar to those of **2a** except that the OAc^- peak is absent and absorptions around the phenyl region are more intense. Integration of the peaks due to H^1 and H^2 relative to the internal reference ($CHCl_2CHCl_2$) indicated a ca. 20% yield of the dialkylthallium(III) species. GLC and ^{1}H NMR analyses of the filtrate showed formation of styrene (29%) and PhCH(OMe)CH_2SPh (26%), the identification of the latter being confirmed by an authentic sample prepared from styrene and ClSPh in CH_2Cl_2–methanol; ^{1}H NMR ($CDCl_3$) δ 3.21 (s, OMe), 3.0–3.45 (m, CH_2), 4.30 (dd, J_H = 5.0 and 7.5 Hz, CH<), 7.0–7.5 (m, Ph). The methine signal was used to determine the stereochemical change in the deuterium-containing product from *erythro*-**1a**-*d* and NaSPh. The reaction of **1e** with $NaCH(COMe)_2$ (1:2) in CD_3OD was followed by ^{1}H NMR spectroscopy to show ca. 90% yield formation of the diphenylthallium(III) species and

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(14) The reaction of aryllead(IV) triacetates with β-dicarbonyl anions resulted in the high yield C–C bond formation.[15]
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(16) Uemura, S.; Tabata, A.; Okano, M. *J. Chem. Soc., Chem. Commun.* **1972**, 517.
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a small amount of benzene after 2 h.

^{1}H NMR spectra were measured on a JEOL PS-100 spectrometer operating at 100 MHz.

Registry No. *erythro*-**1a**-*d*, 75276-79-8; *threo*-**1a**-*d*, 75276-80-1; (*E*)-**1c**, 80515-36-2; (*Z*)-**1c**, 80515-37-3; **1d**, 55073-66-0; **1e**, 20425-82-5; **2a**-*d*, 80515-38-4; (*E*,*E*)-**2c**, 80515-39-5; (*Z*,*Z*)-**2c**, 80515-40-8; **2d**, 50795-46-5; diphenylthallium(III)$^+$, 16785-98-1; Tl(PhCH(OMe)-$CH_2)_2^+$, 80533-28-4; (*E*)-PhCH=CH, 6783-05-7; (*Z*)-PhCH=CHB-$(OH)_2$, 60806-02-2; (*Z*)-PhCH=CHBr, 588-73-8; $Tl(OAc)_3$, 2570-63-0; $B(OAc)_3$, 121-43-7; $P(OMe)_3$, 121-45-9; NaSPh, 930-69-8; NaCH-$(COMe)_2$, 1543-71-9.

Regiochemistry of Nucleophilic Addition to MeC≡CCO$_2$Et π Coordinated to Iron. Synthesis and Structural Characterization of (η^5-C$_5$H$_5$)Fe(CO)(PPh$_3$)(σ-C(CO$_2$Et)=CMe$_2$)

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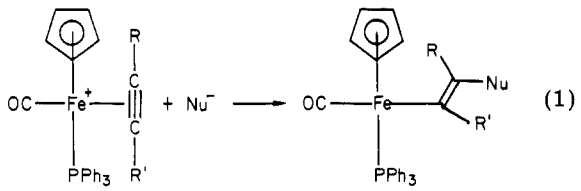
The reaction of $LiMe_2Cu$ and $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(\eta^2\text{-}MeC{\equiv}CCO_2Et)]BF_4$ yields $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(\sigma\text{-}C(CO_2Et){=}CMe_2)$ as proven by an X-ray structural determination. The structure is made up of isolated molecules separated by ordinary van der Waals distances. The Fe atom is four coordinate with CO, PPh_3, Cp, and the fourth coordination site made up of an Fe–C σ bond to the *gem*-dimethyl alkene. The Fe–C distance of 2.030 (2) Å is indicative of a single bond, a result expected from the orientation of the alkene relative to the rest of the iron substituents. The Fe–C(CO) distance is 1.724 (4) Å, and the Fe–P distance is 2.224 (1) Å. The molecule is very compact and the orientation of the ester group is largely determined by the triphenylphosphine moiety. The regiochemistry of the addition reaction seems to be dominated by the electronic influence of the ester group although the overall geometry of the entire complex may also be important. Crystal data: triclinic, $P\bar{1}$, a = 10.333 (4) Å, b = 17.750 (3) Å, c = 8.334 (7) Å, α = 96.66 (3)°, β = 109.05 (6)°, γ = 104.81 (2)°, ρ_{obsd} = 1.27 g/cm^3, ρ_{calcd} = 1.31 g/cm^3, Z = 2, λ = 0.71073 Å, NO = 6501, NV = 325, R_{final} = 0.057. Structure refined by full-matrix least squares including anisotropic temperature factors and anomalous dispersion corrections.

Introduction

The addition of nucleophiles to alkenes π coordinated to a transition metal is a well-developed method for the synthesis of alkylmethyl complexes.[1] Only recently has this approach been extended to the synthesis of alkenylmetal complexes starting from π-alkyne derivatives.[2] An example is shown in eq 1 for an iron system developed by



(1)

some of us.[2a,c] A very important question that needs to be answered is what factors will determine the regiochemistry of the addition reaction for unsymmetrical alkynes (R ≠ R′). This problem has been partially addressed for π-alkene complexes[3] and is the subject of a recent theoretical paper.[4] Trends for alkene and alkyne complexes should be similar for cases in which the alkyne is viewed as a two-electron donor. In fact, alkynes offer a simplification of the problem because, assuming free rotation about the alkyne single bonds, the π-metal complexes would have a local mirror plane containing the metal, the C≡C atoms, and at least the adjacent carbon atoms. In contrast, (π-alkene)metal complexes would have such a local mirror plane only with *geminal* substitution. We present here the synthesis and definitive characterization by X-ray crystallography of the product obtained in the reaction of $LiMe_2Cu$ and $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(\eta^2\text{-}MeC{\equiv}CCO_2Et)]BF_4$. The results establish the regiochemistry of the addition reaction for the interesting case of an alkyne containing an electron-withdrawing substituent. This is a particularly informative case because these results can be compared to the same addition reaction with the free alkyne.[5]

Experimental Section

Preparation of (η^5-C$_5$H$_5$)Fe(CO)(PPh$_3$)[C(CO$_2$Et)C(Me)$_2$]. All of the following procedures were carried out under an inert atmosphere using solvents that were dried and degassed. CH_2Cl_2 (30 mL) was added to a flask containing $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)I$ (1.0 g, 1.8 mmol), $AgBF_4$ (0.36 g, 1.9 mmol), and MeC≡CCO$_2$Et (0.25 g, 2.2 mmol). The solution was stirred at room temperature until a deep red color appeared and immediately cooled to −78 °C. The solution was filtered cold (−78 °C) through filter-aid on a medium glass frit, and the solvent was evaporated below 0 °C. Tetrahydrofuran (THF, 30 mL) chilled to −78 °C was added by cannula tubing to the prechilled residue. A chilled solution of freshly prepared $LiCuMe_2$ (0.18 g, 1.8 mmol) in THF (20 mL) was

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