85 °C (±0.5 °C). The reaction proceeded for 72 h at which time GC analysis showed 100% reduction to deuterated tetrahydroquinoline. The reaction mixture was then passed through a 10-cm Florosil column to remove the catalyst (along with traces of unreduced **1**) and the solvent removed on a rotary evaporator. The sample was redissolved in CDCl$_3$ and its 200-MHz ^{1}H NMR spectrum taken, giving multiplets at 1.95 (H-3), 2.75 (H-4), 6.50 (H-8), 6.62 (H-5), and 7.00 ppm (H-6,7). The H-2 signal was observed at 3.25 ppm as a small peak superimposed on the broad H-1 signal (the one position is initially deuterated but exchanges D for H rapidly during workup). The areas of these peaks (normalized) were as follows: H-2, 0.18; H-3, 1.0; H-4, 1.0; H-5, 1.0; H-6,7, 2.0; H-8, 0.22. These data indicate 1.0 deuterium each at positions 3 and 4, an average of 1.8 deuteriums at position 2, and an average of 0.8 deuterium at position 8.

Partial Reduction of 1 with Deuterium. The experimental conditions were the same as those described in the previous experiment. The reaction was stopped after 150 min, at approximately 50% conversion. Hydrogen chloride gas was bubbled through the reaction mixture to precipitate the unreduced quinoline and the product tetrahydroquinoline. The reaction mixture was then extracted with 50 mL of water; the water extract was make alkaline with excess KOH and extracted with benzene. The benzene extract was dried with anhydrous sodium sulfate and the solvent removed by rotary evaporation. The resulting mixture of quinoline and tetrahydroquinoline was dissolved in CDCl$_3$ and its 200-MHz ^{1}H NMR spectra taken.

The 200-MHz ^{1}H NMR spectrum revealed signals for tetrahydroquinoline at 1.95 (H-3), 2.75 (H-4), 3.25 (H-2), 6.44 (H-8), 6.61 (H-5), and 6.97 ppm (H-6,7). The areas of these peaks (normalized) were as follows: H-2, 0.15; H-3, 1.0; H-4, 1.0; H-5, 1.0; H-6,7. 2.0; H-8, 0.80. These data indicate 1.0 deuterium each at positions 3 and 4, an average of 1.8 deuteriums at position 2, and an average of 0.2 deuterium at position 8.

The signals for quinoline, all of which were downfield of tetrahydroquinoline, were not as well resolved. Signals that could be unambiguously assigned, by decoupling, were at 7.36 (H-3), 7.53 (H-4), and 8.91 ppm (H-2). These signals were in the ratio of 1:1:0.5, indicating an average of 0.5 deuterium at position 2.

Deuteration of 8. A 0.1-mmol sample of (PPh$_3$)$_3$RuCl$_2$ and 1.0 mmol (125 μL) of **8** were placed in the reactor with 20 mL of benzene. The system was pressurized to 150 psi with deuterium gas and placed in the oil bath at 85 °C (±0.5 °C). The reaction proceeded for 270 min, followed by passing the reaction mixture through a 10-cm Florosil column to remove the catalyst, and the solvent was removed on a rotary evaporator. The sample was redissolved in CDCl$_3$ and its 200-MHz ^{1}H NMR spectrum taken, giving multiplets at 1.95 m (H-3), 2.75 (H-4), 3.28 (H-2), 6.49 (H-8), 6.62 (H-5), and 6.98 ppm (H-6,7). The areas of these peaks (normalized) were as follows: H-2, 0.17; H-3, 2.0; H-4, 2.0; H-5, 1.0; H-6,7, 2.0; H-8, 0.89. These data indicate an average of 1.8 deuteriums at position 2 and 0.11 deuterium at position 8. A mass spectrum was also obtained for this compound, with a base peak of m/e 135, and indicated d_1, d_2, and d_3 products.

NMR of Mixture of (PPH$_3$)$_3$RuHCl and 8. A 0.80-g (0.83-mmol) sample of (PPh$_3$)$_3$RuHCl, which was prepared by standard methods,[8a,b] was dissolved in 0.4 mL of dry CDCl$_3$ in an NMR tube, followed by addition of 0.1 mL (0.83 mmol) of **8**, while under an argon atmosphere. An immediate color change from red-violet to brown occurred upon the addition of **8**, the NMR tube was warmed to 35 °C for several hours to ensure completion of any reaction. A 200-MHz ^{1}H NMR of this sample was obtained, giving signals for **8** at 1.91 (pentuplet, H-3), 2.73 (t, H-4), 3.25 (t, H-2), and 5.03 ppm (br, H-1). In the aromatic region signals for **8** were found at 6.53 (d, H-8), 6.63 and 6.82 (both t, H-6,7), and 6.93 ppm (d, H-5). Signals for triphenylphosphine were found in the region from 7.0 to 7.3 ppm. There were no signals observed upfield of Me$_4$Si.

Acknowledgment. We wish to thank Dr. Heinz Heinemann of LBL for continued encouragement and support of our catalysis program. J.L.T. was a DOE summer cooperative student research associate, June–September, 1983. This study was jointly funded by the Director, Office of Energy Research, Office of Basic Energy Science, Chemical Sciences Division, and the Assistant Secretary of Fossil Energy, Office of Coal Research, Liquefaction Division of the U.S. Department of Energy, through the Pittsburgh Energy Technology Center under Contract No. DE-AC03-76SF00098.

Registry No. **1**, 91-22-5; **2**, 85-02-9; **3**, 230-27-3; **4**, 260-94-6; **5**, 229-87-8; **6**, 11095-43-5; **7**, 120-72-9; (PPh3)3RuClH, 55102-19-7; 1,2,3,4-tetrahydroquinoline, 635-46-1; 1,2,3,4-tetrahydro-5,6-benzoquinoline, 40174-35-4; 1,2,3,4–tetrahydro-7,8-benzoquinoline, 5223-80-3; 9,10-dihydroacridine, 92-81-9; 9,10-dihydrophenanthridine, 82692-08-8; 2,3-dihydrobenzothiophene, 4565-32-6; 2,3-dihydroindole, 496-15-1.

Reactions of Chromium Carbene Complexes with 1-Azirines. Synthesis of *N*-Vinylimidates

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Received April 2, 1985

Sunlight irradiation of pentacarbonyl(methoxymethylcarbene)- and pentacarbonyl(methoxyphenylcarbene)chromium(0) complexes in the presence of a number of 2-phenyl-1-azirines produced *N*-vinylimidates in fair to good yield.

Introduction

A variety of transition metals are reactive toward aryl azirines effecting ring-opening processes and producing larger ring heterocycles. Group 6 metal carbonyls dimerize 1-azirines to 1,4-pyrazines or their dihydro derivatives,[1] as does [CpFe(CO)$_2$]$_2$.[2] Azirines having formyl, imino, or vinyl groups undergo ring expansion reactions to form five-membered heterocycles when treated with molybdenum hexacarbonyl.[3] This same complex catalyzes the addition of dimethyl acetylenedicarboxylate to aziridines to give pyrroles.[4] Both Co$_2$(CO)$_8$[5] and [Rh(CO)$_2$Cl]$_2$[6]

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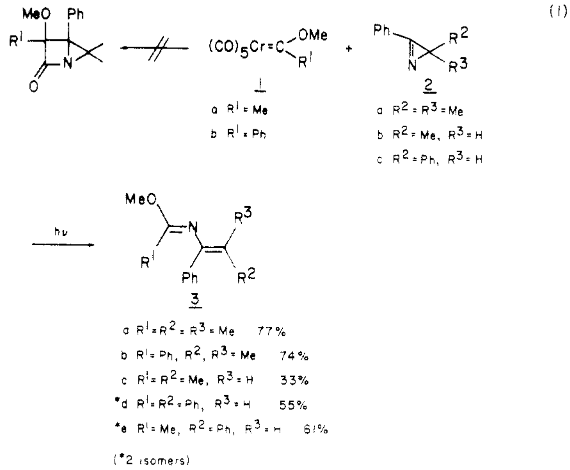
catalyze the conversion of 2-phenylazirine to 2-styrylindole, while palladium(0) complexes convert 2-phenylazirine to bicyclic β-lactams in the presence of carbon monoxide.[7] Finally, molybdenum hexacarbonyl promotes the reaction between azirines and stabilized carbanions to form succinimides.[8]

We have recently developed the photolytic reaction of group 6 metal carbene complexes with imines to produce β-lactams.[9] Azirines would be particularly interesting substrates for this type of reaction, both because of the inherent ring strain and because of the possibility of chemical behavior not observed with acyclic imines. Herein we report the reactions of chromium carbene complexes with 1-azirines under photolytic conditions.

Results and Discussion

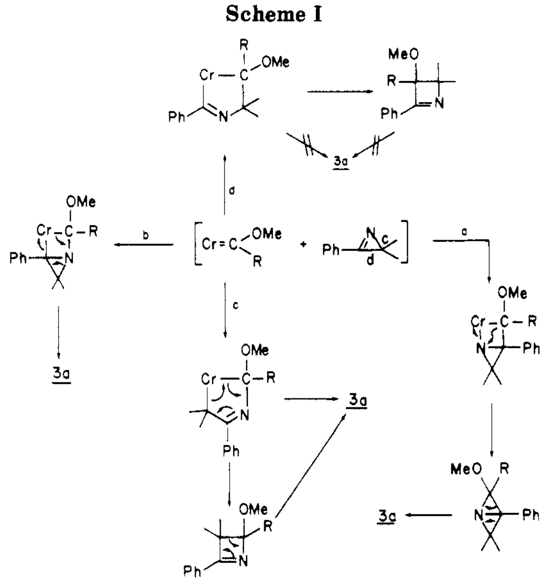
Irradiation of 2-phenyl-1-azirines and pentacarbonyl(methoxymethylcarbene)- or pentacarbonyl(methoxyphenylcarbene)chromium(0) with visible light produced *N*-vinylimidates rather than the expected β-lactams (eq 1). Compounds **3a–c** were obtained as single isomers, even though the possibility of isomers about both double bonds exists. The stereochemistry of these single isomers could not be assigned from the available physical data. In contrast, compounds **3d** and **3e**, both arising from 2,3-diphenyl-1-azirine, were obtained as a 3:1 and 5:1 mixture of two isomers, respectively. These two compounds showed two sets of ^{1}H NMR peaks for the O–Me group (δ 3.97 and 4.13 for **3d** and δ 3.76 and 3.98 for **3e**) and two sets of peaks for the single vinyl proton (δ 5.73 and 6.25 for **3d** and δ 5.91 and 6.36 for **3e**). Again the stereochemistry of these isomers could not be assigned. In addition to complete physical data, including elemental analysis, consistent with the assigned structures, compound **3a** was hydrolyzed to produce isobutyrophenone, as expected, and was synthesized by the alternate route of photolysis of benzonitrile with 2-methyl-3-methoxy-2-butene.[10]

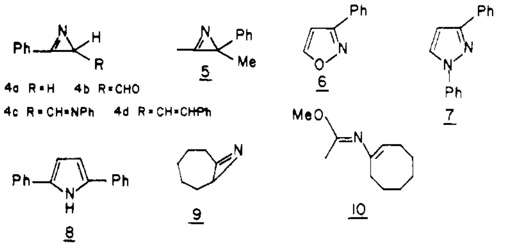


(1)

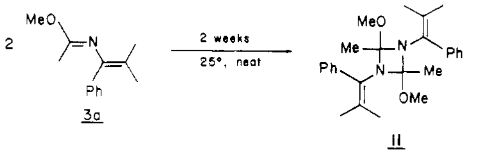
Although several other azirines underwent reaction with chromium carbene complexes, they did not produce appreciable quantities of *N*-vinylimidates. Thus, azirines **4a** and **5** were consumed in the reaction, but an intractable mixture of unidentified products was obtained. Azirines **4b**, **4c**, and **4d** were converted in modest yield to 2-phenyloxazole (**6**), 1,3-diphenylpyrrazole (**7**), and 2,5-diphenylpyrrole (**8**), respectively. However, these *same* products result from the Mo(CO)$_6$-catalyzed reactions of azirines 4b–d,[3] and from their thermolysis at high temperatures,[10] so their production may be unrelated to any reaction involving the carbene complex itself. Fused ring azirine **9** was converted to *N*-vinylimidate **10** in very low yield (7%).

Scheme I





Imidates **3a–e** were all oils, even when analytically pure. However, upon standing several weeks they changed into sharp-melting crystalline solids. The compound resulting from **3a** was most extensively characterized. Although it had the same number of peaks in both the ^{1}H and ^{13}C NMR spectra, *all* chemical shifts were different from those of **3a**. The elemental analysis of the solid material showed it to have the same elemental composition as **3a**. However, chemical ionization mass spectroscopy showed the material had a molecular weight exactly twice that of **3a**. The most likely structure for this solid material is the symmetrical cyclic dimer **11** (eq 2), which, by NMR, is a single isomer as was its precursor **3a**.



(2)

A number of different reaction processes could result in the formation of thee observed *N*-vinylimidates (Scheme I). Cycloaddition of the imine to the carbene in the manner thought to be involved in β-lactam formation (path a) would lead to a metallacycle that cannot directly fragment to **3a**. Reductive elimination to the azabicyclobutane followed by fragmentation would produce **3a**. Cycloaddition in the opposite sense (path b) would produce a

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metallacycle that could directly fragment to **3a**. Alternatively, transition metals are known to insert into the C–N single bonds of azirines.[1-8] Cycloaddition into bond c with either regiochemistry (only one is shown) would produce a five-membered metallacyclic which could directly fragment to **3a** or reductively eliminate to the azacyclobutene, which itself could fragment to **3a**. In contrast, cycloaddition into bond d would result in intermediates that could not lead to **3c**. Which, if any, of these processes is involved in the formation of *N*-vinylimidates **3a–e** is currently under investigation.

Experimental Section

General Procedure. All melting points were obtained with a Mel-Temp melting point apparatus and are uncorrected. Infrared spectra were recorded on a Beckman 4240 spectrophotometer. All 60-MHz ^{1}H NMR spectra were recorded on a Varian Model T-60 spectrometer using Me_4Si as an internal standard and are reported in δ. High-field NMR and ^{13}C NMR spectra were recorded on an IBM WP270sy spectrometer. Mass spectra were recorded on a V. G. Micromass 16F spectrometer.

All chromatographic isolations were accomplished by radial-layer chromatography, using a Chromatotron Model 7294 with Kiesel gel PF silica gel. Analyses were performed by M-H-W Laboratories.

General Procedure for the Synthesis of Vinylimidates through the Photolytic Reaction of 1-Azirines with Chromium Carbene Complexes. 1-Azirine was weighed into a Pyrex 100-mL Erlenmeyer flask which was then sealed with a rubber serum cap. The flask was evacuated and filled with argon (three cycles). The degassed solution of $(CO)_5Cr{=}C(X)(Y)$ (X = OMe: Y = Me, Ph) in distilled petroleum ether (50 mL/mmol) was introduced into the flask which contained 1-arizine under argon by means of a cannula. The reaction vessel was then either placed in a sunny spot outdoors at ambient temperature or irradiated with four 20-W Vitalite fluorescent tubes. After *x* h the solution became heterogeneous and darkened in color. The end point was determined to be when no 1-arizine could be detected by TLC. After filtration, the filtrate was exposed to air under irradiation until the solution became clear and colorless, and a great deal of precipitate had formed. Filtration and removal of solvent in vacuo afforded the desired, in most cases, quite pure vinylimidate, which was further purified by chromatography or by bulb-to-bulb distillation.

Synthesis of (1-Methoxyethylidene)(1-phenyl-2-methylpropenyl)amine (3a). A solution of pentacarbonyl(methoxymethylcarbene)chromium(0) (**1a**)[12] (250 mg, 1.00 mmol) in distilled petroleum ether (50 mL), was introduced into a capped Erlenmeyer flask containing 3,3-dimethyl-2-phenyl-1-azirine (**2a**)[13] (193 mg, 1.00 mmol) under argon. The resulting solution was irradiated until no azirine was detected by TLC (ca. 24 h). After 10-min irradiation the mixture was brown and heterogeneous. Filtration, oxidation, and removal of solvent afforded quite pure product, which was further purified by distillation in a bulb-to-bulb apparatus at 67 °C and 0.5 mm to give a colorless oil (158 mg, 77%).

^{1}H NMR ($CDCl_3$): δ 7.29 (s, 5, aromatic), 3.74 (s, 3, OCH_3), 1.78 (s, 3, CH_3), 1.77 (s, 3, CH_3), 1.68 (s, 3, CH_3). IR (neat): 1680 (C=N) cm^{-1}. Anal. Calcd for $C_{13}H_{17}NO$: C, 76.81; H, 8.43; N, 6.89. Found: C, 76.64; H, 8.21; N, 6.65. Mass spectrum: *m/e* 203 (parent), 188, 172, 146, 129.

Synthesis of (1-Methoxyethylidene)(1-phenyl-2-methylpropenyl)amine (3a) by Photochemical Cycloaddition of Benzonitrile to an Alkene. Compound **3a** was also synthesized by extending the photochemical cycloaddition of benzonitrile to 1,1-dimethoxy-2,2-dimethylethylene[11] to 2-methoxy-3-methylbut-2-ene.[14] A solution of benzonitrile (1.0 g, 10 mmol) and 2-methoxy-3-methylbut-2-ene (3.2 g 32 mmol) in distilled hexane (20 mL) was put in a quartz tube under argon with a balloon. The tube then was placed in a Hanovia 450-W medium-pressure mercury arc lamp photochemical reactor and irradiated for 12 h. The resulting light yellow solution was distilled to recover 2-methoxy-3-methylbut-2-ene; then the residue was evaporated to give a yellow liquid which was separated by Chromatotron (silica gel, 3:1 hexane/ether) to get **3a** (320 mg, 16%).

Synthesis of (α-Methoxybenzylidene)(1-phenyl-2-methylpropenyl)amine (3b). The procedure described for the synthesis of **3a** was used starting with 300 mg (0.96 mmol) of pentacarbonyl(methoxyphenylcarbene) chromium(0) (**1b**)[13] and **2a** (193 mg, 1.00 mmol). After chromatography 187 mg (74%) of pure product was obtained as a colorless oil.

^{1}H NMR ($CDCl_3$): δ 7.36–7.14 (m, 10, aromatic), 3.92 (s, 3, OCH_3), 1.69 (s, 3, CH_3), 1.63 (s, 3, CH_3). IR (neat): 1657 (C=N) cm^{-1}. Anal. Calcd for $C_{18}H_{19}NO$: C, 81.48; H, 7.22; N, 5.28. Found: C, 81.64; H, 7.11; N, 5.24.

Synthesis of (1-Methoxyethylidene)(1-phenylpropenyl)amine (3c). The procedure described for the synthesis of **3a** was used starting with 179 mg (1.00 mmol) of 3-methyl-2-phenyl-1-arizine (**2b**).[15] Removal of petroleum ether in vacuo left quite pure product which was further purified by bulb-to-bulb distillation (70 °C, 0.05 mm) to give 60 mg (33%) of a colorless oil.

^{1}H NMR (CCl_4): δ 7.42 (s, 5, aromatic), 5.05 (q, J = 7 Hz, 1, H), 3.80 (s, 3, OCH_3), 1.95 (s, 3, CH_3), 1.87 (d, J = 7 Hz, 3, CH_3). IR (neat): 1670 (C=N) cm^{-1}. Anal. Calcd for $C_{12}H_{15}NO$: C, 76.16; H, 7.99; N, 7.40. Found: C, 76.23; H, 7.87; N, 7.36.

Synthesis of (α-Methoxybenzylidene)(1-phenyl-2-phenylpropenyl)amine (3d). The same procedure described for the synthesis of **3a** was used starting with **2c**[16] (193 mg, 1.00 mmol) and **1b** (300 mg, 0.96 mmol). After chromatography 172 mg (55%) of pure product was obtained as a yellow oil which contains two isomers.

^{1}H NMR ($CDCl_3$): δ 7.5–6.9 (m, 5, aromatic), 6.25, 5.73 (s, 1, H), 4.13, 3.97 (s, 3, OCH_3). IR (neat): 1657 (C=N) cm^{-1}. Anal. Calcd for $C_{22}H_{19}NO$: C, 84.32; H, 6.11; N, 4.47. Found: C, 84.43; H, 6.02; N, 4.41.

Synthesis of (1-Methoxyethylidene)(2-phenyl-2-styryl)amine (3e). The procedure described for the synthesis of **3a** was used starting with 193 mg (1.00 mmol) of 2,3-diphenyl-1-azirine (**2c**). Removal of petroleum ether in vacuo left quite pure product as a solid which was purified by distillation in a bulb-to-bulb apparatus at 130 °C and 0.5 mm to give 154 mg (61%); mp 78 °C.

^{1}H NMR ($CDCl_3$): δ 7.07–7.30 (m, 10, aromatic), 5.91 (s, 1, CH), 3.76 (s, 3, OCH_3), 2.03 (s, 3, CH_3). IR (neat) 1670 (C=N) cm^{-1}. Anal. Calcd for $C_{17}H_{17}NO$: C, 81.24; H, 6.82; N, 5.57. Found: C, 81.34; H, 6.77; N, 5.63.

Hydrolysis of 3a. To **3a** (0.1 g) was added 1.5 mL of methanol and 5.0 mL of 20% aqueous HCl. After being stirred for 16 h at room temperature, the mixture was poured into 25 mL of water and extracted with 75 mL of ether in three portions. The combined ether layers were washed with water and dried over $MgSO_4$. Evaporation of the filtrate afforded a colorless liquid which had NMR and IR spectra identical with those of isobutyrophenone.

Dimerization of 3a. Either pure **3a** or the solution of **3a** in the reaction mixture was allowed to stay exposed to air for about 20 days at room temperature. The pure **3a** became a solid. Evaporation of the **3a** solution also afforded the same solid which was recrystallized from hexane, to give square crystals, mp 85.5 °C.

^{1}H NMR ($CDCl_3$): δ 7.92, 7.45 (2 m, 5, aromatic), 3.27 (s, 3, OCH_3), 1.70 (s, 3, CH_3), 1.68 (s, 3, CH_3), 1.64 (s, 3, CH_3). IR (KBr): 1620 cm^{-1}. Anal. Calcd for $C_{13}H_{17}NO$: C, 76.81; H, 8.43; N, 6.89. Found: C, 76.69; H, 8.34; N, 6.76. ^{13}C NMR: δ 26.42, 26.80, 27.64, 49.31, 87.84, 122.67, 128.48, 128.63, 130.38, 131.23, 175.47. NH_3 chemical ionization mass spectrum: *m/e* 406 (parent), 405, 374 (P – OMe).

Synthesis of (1-Methoxyethylidene)-1-cyclooctenеamine (10). The procedure described for the synthesis of **3a** was used starting with 123 mg (1.00 mmol) of 9-azibicyclo[6.1.0]non-1(9)-ene (**9**).[17] After Chromatotron purification only 13 mg (7%) of **10** was obtained.

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^1H NMR ($CDCl_3$): δ 4.7 (t, 1, H), 3.65 (s, 3, OCH_3), 1.57–2.17 (m, 15, CH_3, CH_2). IR (neat): 1695 cm^{-1}.

This material was not further purified.

Reaction of Vinyl-Substituted Azirines 4b–d with Chromium Carbene Complexes. These reactions were run in the usual manner, using 1 mmol of the azirine[10] and 1 mmol of the methoxymethylcarbene complex. Oxidation of the crude material followed by purification by radial layer chromatography gave **6** (50 mg, 31%), **7** (61 mg, 28%), or **8** (124 mg, 57%), respectively. Infrared, NMR, and mass spectra as well as melting points were identical with those reported for these compounds.[10]

Acknowledgment. Support for this research under Grant No. 2RO1GM21178-06 from the National Institutes of General Medical Sciences (PHS) is gratefully acknowledged. C. Y. thanks the Chendgu Institute of Organic Chemistry, Peoples Republic of China, for financial support. A. K. acknowledges the Schweizerische Nationalfonds zur Foerderung der wissenschlaftichen Forschung for partial financial support.

Registry No. **1a**, 20540-69-6; **1b**, 27436-93-7; **2a**, 14491-02-2; **2b**, 16205-14-4; **2c**, 16483-98-0; **3a**, 97704-60-4; **3a** dimer, 97719-87-4; **3b**, 97704-61-5; **3c**, 97704-62-6; **3d**, 97704-63-7; **3e**, 97704-64-8; **4b**, 42970-55-8; **4c**, 52179-65-4; **4d**, 90382-67-5; **6**, 1006-65-1; **7**, 4492-01-7; **8**, 838-40-4; **9**, 97704-65-9; **10**, 97719-88-5; benzonitrile, 100-47-0; 2-methoxy-3-methylbut-2-ene, 26578-81-4; isobutyrophenone, 611-70-1.

Reactivity and Ligand Exchange in Triplatinum Clusters

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Received February 15, 1985

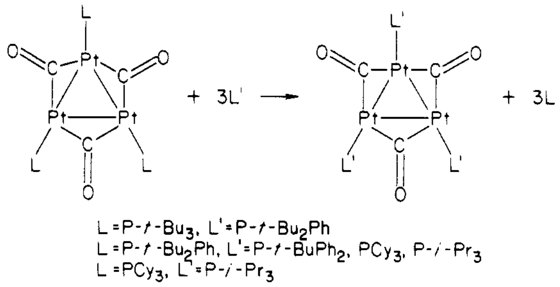
The phosphine ligands, L, in the triplatinum clusters $Pt_3(CO)_3L_3$ have been found to undergo a facile ligand substitution reaction with 3 equiv of L′ to give $Pt_3(CO)_3L'_3$ where L = P-*t*-Bu_3 and L′ = P-*t*-Bu_2Ph, L = P-*t*-Bu_2Ph and L′ = P-*t*-$BuPh_2$, PCy_3, and P-*i*-Pr_3, and L = PCy_3 and L′ = P-*i*-Pr_3. The substitution occurs by an associative mechanism with the Pt_3 triangle remaining intact during the process. Mixtures of $Pt_3(CO)_3$(P-*t*-$Bu_2Ph)_3$, **1**, and either $Pt_3(^{13}CO)_3$(P-*t*-$Bu_2Ph)_3$ or $Pt_3(CO)_3(PCy_3)_3$, **2**, scramble both phosphine and carbonyl ligands in a much slower reaction (approximately 1 h at 25 °C whereas L′ substitution occurs in about 25 s). Reactions of the cluster **1** with CS_2, OCS, and SO_2 also have been examined. In all cases, fragmentation of the trimer occurs to give dimeric products. The reaction of **1** and CS_2 results in formation of either $Pt_2(\mu\text{-}CS_2)_2$(P-*t*-$Bu_2Ph)_2$ or $Pt_2(\mu\text{-}S)(CO)_2$(P-*t*-$Bu_2Ph)_2$, **4**, depending on reaction conditions, whereas **4** is obtained from the reaction of **1** with OCS. Treatment of **1** with SO_2 at 25 °C gives $Pt_2(\mu\text{-}SO_2)(CO)_2$(P-*t*-$Bu_2Ph)_2$, **5**, which on prolonged standing in solution at 25 °C converts to the triplatinum cluster $Pt_3(CO)_2(SO_2)$(P-*t*-$Bu_2Ph)_3$, **6**. ^{31}P NMR spectroscopy reveals that the initial reaction gives mixtures of **5**, **6**, and $Pt_3(SO_2)_2(CO)$(P-*t*-$Bu_2Ph)_3$.

Introduction

The reactivity of transition-metal cluster compounds is an area of continuing interest in organometallic chemistry.[1,2] An understanding of the reactions that such systems undergo is essential for any evaluation of their potential as catalysts. We have been studying the chemistry of the triplatinum cluster $Pt_3(\mu\text{-}CO)_3L_3$, where L is a bulky phosphine ligand. While a number of these clusters have been synthesized[3] and characterized by NMR spectroscopy[4] and X-ray crystallography,[5] very little has been reported about their reactivity.

In 1970 Chatt and Chini reported[6] the synthesis of the clusters $Pt_3(CO)_3L_4$, L = PPh_3, PPh_2Me, and PPh_2Et, and $Pt_3(CO)_3L_3$, L = $PPh_2(CH_2Ph)$, by the decomposition of the mononuclear carbonyl compounds $Pt(CO)_2L_2$. They noted that the addition of free phosphine to the trinuclear clusters immediately generates monomeric species which led them to assume a possible equilibrium between $Pt_3(CO)_3L_4$ and $Pt_3(CO)_3L_3$ plus L, followed by cluster breakdown. This equilibrium has been confirmed by ^{31}P NMR studies.[4b] Shortly thereafter the analogous palladium cluster, $Pd_3(CO)_3(PPh_3)_4$ was reported.[7] This cluster reacts with an excess of PPh_3 to give $Pd(CO)(PPh_3)_3$, and it also loses a PPh_3 ligand when recrystallized from toluene resulting in formation of the compound $Pd_3(CO)_3(PPh_3)_3$.

Scheme I



Recent work by Briant, Evans and Mingos has shown that the cluster $Pt_3(CO)_3(PPh_3)_4$ reacts with SO_2 to produce the SO_2-substituted compound $Pt_3(\mu\text{-}SO_2)_3(PPh_3)_3$.[8] This is one of a small number of clusters containing the SO_2 ligand although the coordination chemistry of SO_2 has been widely studied.[9] Goel and Goel reported the cluster

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