42.92; H, 3.77; N, 6.83. Found: C, 43.03; H, 3.95; N, 6.84.

Bis(pyridine)oxoosmium(VI) Ester of Skatole. Osmium tetraoxide (0.1 g, 3.93×10^{-4} mol) dissolved in 5 mL of anhydrous diethyl ether was added to an ether solution containing 0.18 mL of pyridine (2.32×10^{-3} mol) and 0.052 g of skatole (3.96×10^{-4} mol). After 1 h of reaction the precipitate was filtered and washed with diethyl ether. This product was then air-dried for 2 h: yield 0.132 g (62%); NMR (CDCl$_3$) δ 1.87 (s, Me), 5.50 (s, 2-H). Anal. Calcd for C$_{19}$H$_{19}$N$_3$O$_4$Os: C, 41.98; H, 3.52; N, 7.73. Found: C, 42.02; H, 3.66; N, 7.62.

Interaction of Cyclopropane with Platinum-Metal Chlorides under Carbon Monoxide Pressure in Benzene

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The six platinum-metal chlorides were reacted with cyclopropane in benzene under carbon monoxide pressure to produce propylbenzenes and, in three instances, chlorobutyrates. The isomer of propylbenzene obtained ranged from pure n-propylbenzene for PdCl$_2$ to pure isopropylbenzene for OsCl$_3$ and IrCl$_3$. The other three platinum-metal chlorides gave mixtures of the two propylbenzenes. The reaction was shown to be specific for benzene and cyclopropane as chlorobenzene and toluene failed to enter into the reaction. Likewise, methylcyclopropane did not react with benzene to produce butylbenzenes.

Platinum and rhodium complexes have been shown to undergo reaction with cyclopropanes to form platinacyclobutanes[1] and rhodiacyclopentanones,[2] respectively. Palladium chloride was reported[3] to react with cyclopropane in benzene under carbon monoxide pressure to produce, upon workup with methanol, a mixture of the three possible methyl chlorobutyrates and n-propylbenzene. The rhodiacyclopentanone 2, obtained by the interaction of [Rh(CO)$_2$Cl]$_2$ with cyclopropane, was thought to occur via CO insertion into the rhodiacyclobutane 1.[2]

If palladium underwent a similar set of insertions as was found for rhodium, then one could possibly envision the formation of the 4-chlorobutyrate as arising from 4 and n-propylbenzene as arising from 3. As this possibility

intrigued us and offered the potential of being characteristic for the platinum metals, we decided to undertake a study of the interaction of cyclopropane with platinum-metal chlorides under carbon monoxide in benzene.

Results

We first reexamined the reaction of cyclopropane with palladium chloride in benzene under 100 atm of carbon monoxide at 90 °C. We found that the ratio of chlorobutyrates (73%) to n-propylbenzene (27%) was similar to that reported earlier.[3] While the formation and ratio of these products was not too dependent upon carbon monoxide pressure and temperature, we did find that the ratio of products was very dependent upon the molar ratio of cyclopropane to palladium chloride. When the molar ratio of cyclopropane to palladium chloride was 1.5:1, n-propylbenzene represented about 27% of the product composition. However, when we increased the molar ratio of cyclopropane to palladium chloride to 30:1, we found that n-propylbenzene now represented greater than 90% of the product mixture. The chlorobutyrates made up the remaining part of the product mixture, and their relative ratios are given in Table III. We found that similar results were obtained by using 15 atm of carbon monoxide at 90 °C, and the remaining experiments reported here were done at this lower pressure.

The yield of n-propylbenzene (based on PdCl$_2$) was 40–50%. Palladium was converted to a mixture of [Pd(CO)Cl$_2$]$_2$ and [Pd$_2$Cl(CO)$_2$]$_n$. These products are the same as those reported for the palladium-mediated carbonylation of ethylene under similar reaction conditions.[4] These palladium complexes could be filtered, washed with benzene, and reused to effect the formation of n-propylbenzene from a fresh charge of benzene, cyclopropane, and

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Table I. Conversion and Percent Composition of Propylbenzenes to Methyl Chlorobutyrates Obtained from the Reaction of Benzene, Carbon Monoxide, and Cyclopropane with Platinum-Metal Chlorides[a]

metal chloride	% conversion[b]	% propylbenzenes[c]	% chlorobutyrates[c]
RuCl3	40	100	0
OsCl3	75	95	5
RhCl3	45	100	0
IrCl3	70	90	10
PdCl2	45	90	10
PtCl2	40	100	0

[a] See the Experimental Section for details of the reaction conditions. [b] Based on metal chloride. [c] The ratio was determined by ¹H NMR.

Table II. Percent Composition of Isomeric Propylbenzenes Obtained from the Reaction of Benzene, Carbon Monoxide, and Cyclopropane with Platinum-Metal Chlorides[a]

metal chloride	% n-propylbenzene[b]	% isopropylbenzene[b]
RuCl3	44	56
OsCl3	0	100
RhCl3	86	14
IrCl3	0	100
PdCl2	100	0
PtCl2	92	8

[a] See the Experimental Section for details of the reaction conditions. [b] The ratio was determined by ¹H NMR.

Table III. Percent Composition of Isomeric Methyl Chlorobutyrates Obtained from the Reaction of Benzene, Carbon Monoxide, and Cyclopropane with Platinum-Metal Chlorides[a]

metal chloride	% 2-chloro[b,c]	% 3-chloro[b,c]	% 4-chloro[b,c]
RuCl3			
OsCl3	40	60	
RhCl3			
IrCl3	67	33	
PdCl2	43	29	28
PtCl2			

[a] See the Experimental Section for details of the reaction conditions. [b] The ratio was determined by VPC using a 10 ft × ¹/₈ in., 10% DEGS on 80/100 Chromosorb G column at 120 °C. [c] No chloro ester was observed for the situations where no percentage is given.

carbon monoxide. The complexes, when prepared independently,[5,6] were also effective in forming n-propylbenzene under the reaction conditions. Yields above 50% could not be obtained in spite of the fact that the palladium complexes formed in the reaction could be used with *fresh* charges of benzene, cyclopropane, and carbon monoxide to produce more product. The reaction could be made catalytic in palladium chloride by the addition of stoichiometric amounts of cupric chloride. In addition, we found that dichlorobis(benzonitrile)palladium(II) was effective in promoting the formation of n-propylbenzene, but palladium acetate was not.

The n-propyl fragment (C_3H_7) of n-propylbenzene has one more hydrogen than is available from simple addition of cyclopropane (C_3H_6) to benzene. We performed several experiments in an attempt to determine the source of the seventh hydrogen. A reaction was run under standard conditions in benzene-d_6, but the n-propyl fragment showed no deuterium incorporation as determined by ¹H NMR.[7] Similarly, workup of the reaction mixture with MeOD did not show any deuterium incorporation either. In a third experiment we carefully vacuum dried our palladium chloride and distilled our benzene from sodium–benzophenone. The reaction vessel was charged in a Vacuum Atmospheres drybox and then run under the standard conditions. We were still able to obtain the normal amount of n-propylbenzene, ruling out protonation by insidious water. These results suggest that the seventh hydrogen may come from another molecule of cyclopropane. At this time, the cost of cyclopropane-d_6 (and remembering that cyclopropane is used in a 29 molar excess) prohibits us from performing this experiment. The fate of a cyclopropane molecule providing this seventh hydrogen is indeed intriguing, to say nothing of how this process may be activated. We have been unable to identify, at this time, any suitable species which suggested that its parentage may have been cyclopropane.

The reaction reported here is amazingly specific for benzene and cyclopropane. Substitution of chlorobenzene or toluene for benzene resulted in no alkylation of the aromatic ring. Likewise, substituting methylcyclopropane for cyclopropane did not result in the formation of any butylbenzenes.

We next sought to determine the effect of other platinum-metal chlorides on this reaction. We employed RuCl3, OsCl3, RhCl3, IrCl3, and PtCl2 in separate experiments under conditions identical with those used with palladium chloride. All of these platinum-metal chlorides produced

propylbenzenes, but none of these were specific for n-propylbenzene as was the case with palladium chloride. In addition, a few of these also produced methyl chlorobutyrates upon workup with methanol (vide infra). Unlike the palladium chloride example, the metal component in these five reactions was converted to a black powder except in the case of rhodium which gave a homogeneous solution from which a small amount of [Rh(CO)₂Cl]₂ could be recovered. This rhodium dimer was likewise effective in converting benzene to propylbenzene under the reaction conditions, but the yield was considerably less than when one started with RhCl3. The results of these reactions are illustrated in Tables I–III.

It was implied earlier that some of the products from these reactions might be rationalized by invoking metallacycle intermediates. The rhodiacyclopentanone 2 is a known compound, and the platinum compound 5 is also known. As both platinum and rhodium chlorides pro-
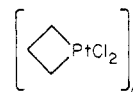
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duced propylbenzenes from benzene and cyclopropane under carbon monoxide pressure, we wondered if we might be able to employ 2 or 5 directly in these reactions without the use of cyclopropane. We attempted both of these experiments but were unsuccessful in obtaining any propylbenzenes or methyl chlorobutyrates. If cyclopropane was added in addition to the complexes 2 and 5, then propylbenzenes were obtained. This does not establish, of course, that metallacycles are involved in the reaction.[8]

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(6) Fischer, E. O.; Vogler, A. *J. Organomet. Chem.* **1965**, *3*, 161.

(7) Mass spectral analysis was also performed on the product and confirmed the ¹H NMR analysis of no deuterium incorporation.

(8) The metallacycles 2 and 5 are both prepared from cyclopropane. These results suggest an experiment employing cyclopropane-d_6 in the preparation of 2 and 5 followed by determination of whether the observed propylbenzenes are labeled or not. We have discussed earlier in this paper the prohibitive cost of cyclopropane-d_6 for us at this time.

Discussion

All of the platinum-metal chlorides proved to be effective in forming propylbenzenes from benzene and cyclopropane. It is interesting that three of the metal chlorides produced only one isomer of propylbenzene (see Table II) while the other three produced a mixture of n-propyl and isopropylbenzene. Furthermore, only three of the metal chlorides will carbonylate cyclopropane under these conditions, and only the palladium chloride reaction produced any of the methyl 4-chlorobutyrate isomer.

Within a group of congeners only palladium and platinum produced n-propylbenzene as the major product. Rhodium favored the n-propyl isomer (86:14) while iridium gave pure isopropylbenzene. Likewise, osmium chloride gave pure isopropylbenzene, but its congener, ruthenium chloride, gave nearly a 1:1 mixture of the two propylbenzene isomers. Also, only one member within a group of congeners produced any chlorobutyrates. There does not appear to be any consistency between the products obtained and the oxidation state or d^n state of the metal.

A prior isomerization of cyclopropane to propylene can account for the production of methyl 3-chlorobutyrate, as propylene substituted for cyclopropane in these reactions gives this isomer. However, only small amounts of propylene can be detected in the reaction mixtures at the end of 20 h.[9] If the conversion of propylene is efficient, then one can still rule out a large conversion of cyclopropane to propylene as the 3-chlorobutyrate isomer represents a very small amount of the product composition. Under the reaction conditions, propylene will react with $OsCl_3$ and $IrCl_3$ to produce small (i.e., demonstrably less than when cyclopropane was used) amounts of isopropylbenzene. However, the methyl 3-chlorobutyrate is now the major product, and the methyl 2-chlorobutyrate was not observed at all. The other four platinum-metal chlorides did not give detectable amounts of propylbenzenes when propylene was substituted for cyclopropane. It would seem clear from these experiments that a cyclopropane to propylene reaction does not play a significant role in producing the products observed from the reaction of cyclopropane and

benzene under carbon monoxide pressure in the presence of platinum-metal chlorides.

The results to date do not give any clear indication as to what the mechanism of this reaction may be or even if one reaction scheme is general for the six platinum-metal chlorides. The results do describe the general production of propylbenzenes from cyclopropane and benzene under carbon monoxide pressure in the presence of platinum-metal chlorides. The results describe interesting variations in isomer distribution, depending upon the metal chloride used. The carbonylation of cyclopropane was found to occur for three of the metal chlorides, and the interesting 2-chlorobutyrate isomer was obtained for all three whereas the 4-chlorobutyrate isomer was obtained only for the palladium chloride reaction. The reactions were also shown to be specific for benzene and cyclopropane.

Experimental Section

Spectra and Analyses. The ^1H NMR spectra were recorded on either a Varian T-60 or a Varian XL-100 spectrometer. The products were isolated by using a 10 ft × $^1/_4$ in., 20% DEGS on 60/80 Chromosorb G column at 80 °C with an Aeorograph A-90-P3 gas chromatograph. In all instances the products were identified by spectroscopic comparison to authentic samples. Analytical work was performed by using a 10 ft × $^1/_8$ in., 10% DEGS on 80/100 Chromosorb G column at 120 °C with a Varian 940 gas chromatograph. The reactions were carried out by using a Parr reaction vessel. The yields and percent composition of products are given in Tables I–III.

General Procedure. A Parr reaction vessel was charged with 250 mL of benzene, 0.5 g of a platinum-metal chloride (Tables I–III), and a 29 molar excess of cyclopropane. The vessel was pressurized with 15 atm of carbon monoxide and then heated to 90 °C for 20 h with stirring. After cooling, the vessel was opened and an excess of methanol (to convert the acid chlorides to methyl esters) was added. The solution was then concentrated in vacuo, and the products were isolated and identified as described above.

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(9) This detection was done by analyzing the benzene solution with an 11 ft × $^1/_8$ in., 20% silver nitrate–ethylene glycol on 80/100 Chromosorb P column. The amount of propylene observed by this method was never more than 2% of the unreacted cyclopropane.