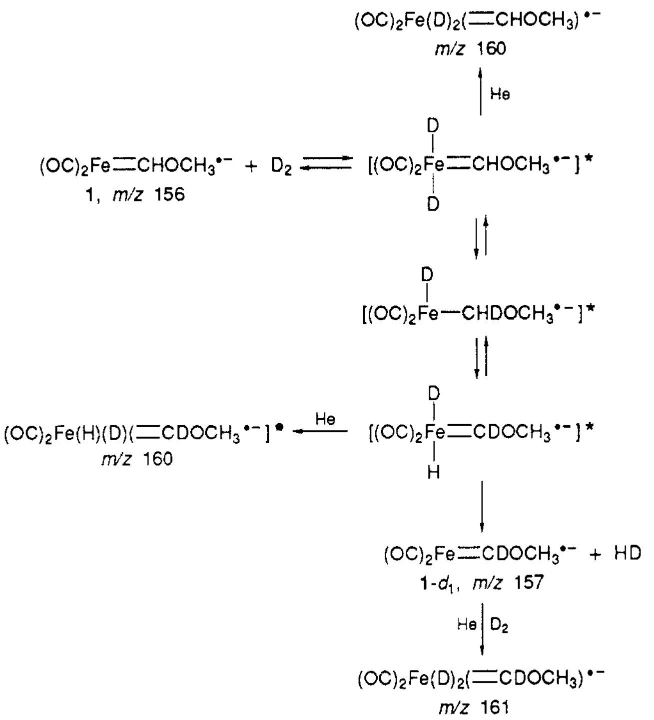
Scheme I



bond followed by expulsion of H_2. The 17-electron hydrido–carbyne structure $(OC)_2Fe(H)(\equiv COCH_3)^{\bullet-}$ (3) was considered to be less probable than 1.

To determine the structure of the m/z 156 ions, the reaction of D_2 with the mixture of m/z 156 and 158 ions from reaction 4 was carried out. Only the m/z 156 ions react yielding two primary negative ion products at m/z 157 (H/D exchange; 23%) and 160 (addition; 77%) and a secondary ion product at m/z 161 (H/D exchange + addition). These results are consistent with 1 being the structure of the (adduct − H_2) ions at m/z 156. If the hydrido–carbyne complex 3 were the structure of the m/z 156 ions, must revert to 1 in the collision–addition with D_2 because the available evidence shows that 17- and 18-electron metal complex negative ions do not react with H_2 or D_2 in the gas phase.[17] The suggested mechanism of the D_2 reactions is shown in Scheme I. Confirmation for the iron–carbene structure 1 was obtained when the reaction of $(OC)_2Fe^{\bullet-}$ with CD_3OCH_3 formed only $(OC)_2Fe{=}CDOCH_3^{\bullet-}$ (m/z 157) and $(OC)_2Fe{=}CHOCD_3^{\bullet-}$ (m/z 159). The absence of reaction of the adduct at m/z 158 (eq 4a) with D_2 is consistent with the 17-electron structure $(OC)_2Fe(H_2)({=}CHOCH_3)^{\bullet-}$ for these ions and rules out the 15-electron structures of the Lewis complex $((OC)_2Fe^{-}(O^{+}(CH_3)_2))^{\bullet-}$ and $(OC)_2Fe(H)(CH_2OCH_3)^{\bullet-}$ where addition, substitution for the ether molecule, or H/D exchange could occur.

The results of the reaction of $(OC)_2Fe^{\bullet-}$ with $(CH_3)_2O$ are the first example of α-hydrogen migration in a gas-phase transition-metal–alkyl negative ion complex. The availability of the 15-electron Fischer-type carbene complex $(OC)_2Fe{=}CHOCH_3^{\bullet-}$ for study is the bonus of this investigation.

Acknowledgment. We gratefully acknowledge the support of this research by the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

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Palladium-Catalyzed Alkyne–Oxalate Ester Reaction. A Formal Carbon–Carbon Bond Cleavage Process

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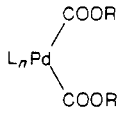
Received February 13, 1989

Summary: Terminal alkynes react with oxalate esters in the presence of bis(dibenzylideneacetone)palladium or palladium acetate and 1,4-bis(diphenylphosphino)butane, at 100 °C and 82 atm of carbon monoxide, to give trans-α,β-unsaturated esters and diynes. This carbon–carbon bond cleavage reaction may be proceeding by oxidative addition of the oxalate ester to palladium.

The palladium complex catalyzed oxidative coupling of carbon monoxide and alcohols to oxalate esters is a reaction of considerable interest.[2,3] It is believed that the oxalate ester arises by reductive elimination from a palladium dicarboxylate such as 1.



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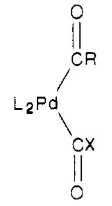

2

Another area which has been the subject of numerous studies in recent years is the palladium[4] and cobalt[5] catalyzed double carbonylation of halides to α-keto acids, esters, and amides. Investigations by Yamamoto and coworkers[4] indicate that the α-dicarbonyl compound is formed by reductive elimination from a acylmetal carboxylic acid, ester or amide (2, X = OH, OR, NR_2). It seemed conceivable to us that, under appropriate conditions, one could attain oxidative addition of the carbon–carbon bond of oxalate esters to palladium resulting in the generation of 1, i.e. the reverse of the above processes. This communication describes the interesting palladium-catalyzed reaction of alkynes and oxalate esters.

No reaction occurs when a mixture of phenylacetylene (3, Ar = Ph) and diethyl oxalate (4, R = C_2H_5) in 1,2-dimethoxyethane (DME) is treated with a catalytic quantity of bis(dibenzylideneacetone)palladium(0) and 82 atm of carbon monoxide, at 100 °C for 3 days. However, the presence of 1,4-bis(diphenylphosphino)butane (dppb) results in the generation of *trans*-methyl cinnamate (5, Ar

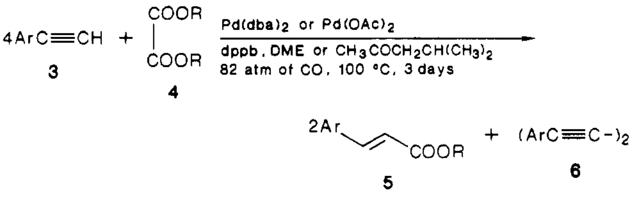

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Table I. Palladium-Catalyzed Alkyne-Oxalate Ester Reactions

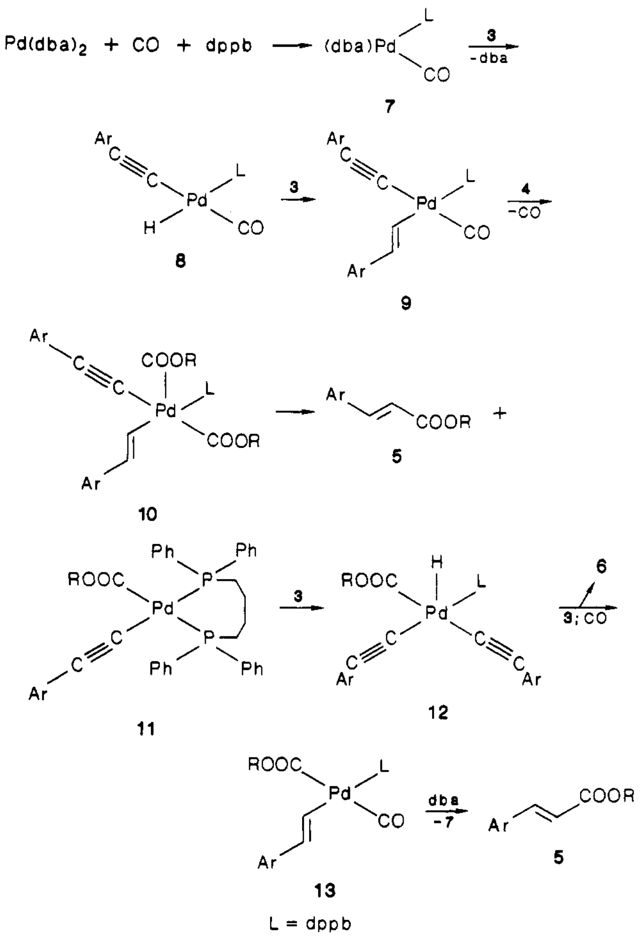
3, Ar =	4, R =	cat.[a]	added ligand	solv[b]	yield,[c] % 5	6
Ph	C_2H_5	A		I		
		A	dppb	I	30	18
		A	PBu_3	I		
		A	diphos	I		
	CH_3	A	dppb	II	57	24
		B	dppb	I	64	48
		B	diphos	I		
	C_4H_9	A	dppb	I	30	nd
	CH_2Ph	B	dppb	II	54	nd
	p-$CH_3C_6H_4$	B	dppb	II	62	nd
p-$CH_3C_6H_4$	C_2H_5	A	dppb	II	32	nd
p-$CH_3OC_6H_4$	CH_3	A	dppb	II	37	nd

[a] A = $Pd(dba)_2$; B = $Pd(OAc)_2$. [b] I = DME; II = 4-methyl-2-pentanone. [c] Products were identified on the basis of IR, NMR (^1H, ^{13}C), and MS determinations and by GC spiking with authentic materials. nd = not determined.

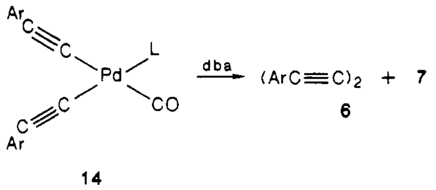
= Ph, R = C_2H_5) in 30% yield and 1,4-diphenylbuta-1,3-diyne (6, Ar = Ph) in 18% yield. The ratio of alkyne to oxalate ester used was 4:1 while that of alkyne/Pd-$(dba)_2$/dppb was 25/1/1. Other bidentate [e.g. 1,2-bis(diphenylphosphino)ethane] or monodentate [e.g. tri-*n*-butylphosphine] phosphines are ineffective for this reaction. Palladium acetate can also be used as the metal catalyst, and 4-methyl-2-pentanone is an alternate solvent to DME. The palladium-catalyzed alkyne–oxalate ester reaction is applicable to a variety of alkyl and aryl oxalates giving trans-α,β-unsaturated esters in reasonable yields, with diynes formed as the accompanying product (see Table I). Internal alkynes including 1-phenyl-1-butyne and 4-methyl-2-pentyne do not react with oxalate esters under these conditions.

Let us consider the mechanism outlined in Scheme I as a working hypothesis for the alkyne–oxalate ester reaction (illustrated with $Pd(dba)_2$). Initial interaction of $Pd(dba)_2$ with carbon monoxide and dppb may give 7 (L = dppb complexed to Pd via one of the two P atoms) which can then react with the carbon–hydrogen bond of the alkyne 3 affording 8. The latter, which is a palladium hydride, can add to the carbon–carbon triple bond of another molecule of alkyne to form 9. Oxidative addition of oxalate ester may then occur to give 10 which, on reductive elimination, affords the ester 5 and complex 11. Reaction of the latter with alkyne may form a new palladium hydride, 12. Complex 12, as 8, can add to the triple bond of the fourth molecule of alkyne, with concurrent reductive elimination of the diyne 6, affording 13. The second molecule of α,β-unsaturated ester (5) may result from 13 with 7 being regenerated in the process. Note that one possible role of carbon monoxide (no reaction occurs in its absence) is to stabilize several of the intermediates (e.g. 7–9) while dppb is capable of functioning as a mono- or bidentate ligand.

Scheme I



An alternate pathway that merits consideration is C–H bond insertion of 8 with another alkyne (rather than Pd–H addition to the triple bond), which results in loss of hydrogen to give 14. The diyne 6 and regenerated 7 can then be formed by reductive elimination. The hydrogen produced in the step leading to 14 could, in principle, react with oxalate ester to give 2 equiv of formate ester. Consequently, it would be the formate ester, by reaction with alkyne, which is responsible for the formation of the α,β-unsaturated ester 5. However, no butyl formate is detected when dibutyl oxalate is treated with either hydrogen or synthesis gas (1:1 CO/H_2), $Pd(dba)_2$, and dppb, in DME at 100 °C and 82 atm for 3 days.



The following general procedure was used: to a stirred mixture of the alkyne (2.5 mmol) and oxalate ester in DME or 4-methyl-2-pentanone (1.5 mL) was added the palladium catalyst (0.1 mmol) and dppb (0.1 mmol). The autoclave was purged with carbon monoxide and then pressurized to 82 atm. After reaction for 3 days at 100 °C, the reactor was cooled to room temperature, and the autoclave was opened. The solution was filtered through Celite, and the filtrate was analyzed by gas chromatography. The products were separated by concentration of the filtrate, followed by purification on thin-layer chromatography (silica gel) using 7:3 ether–hexane as the developer system.

In conclusion, the palladium complex–dppb system is catalytically active for the intriguing reaction of alkynes and oxalate esters. To our knowledge, these are the first examples of a metal-catalyzed oxalate ester reaction involving formal carbon–carbon bond cleavage.

Acknowledgment. We are grateful to British Petroleum and to the Natural Sciences and Engineering Research Council of Canada for support of this research.