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Preliminary Communication

THE INSERTION OF THE DIOXIDES OF CARBON AND SULPHUR INTO THE PALLADIUM-CARBON BOND

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Summary

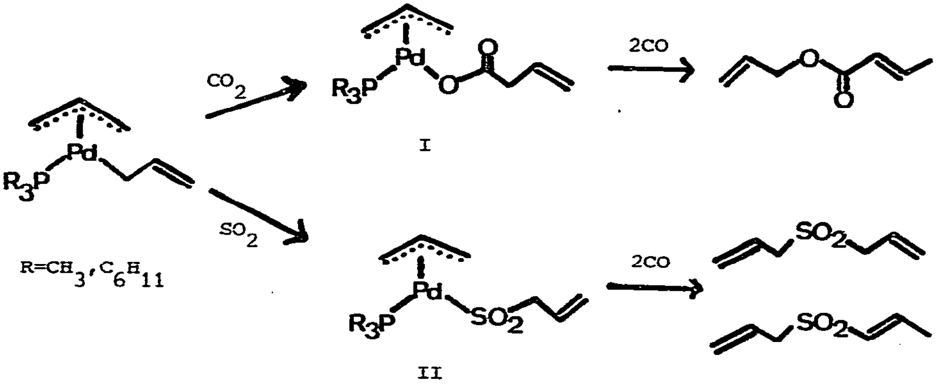
Bis(η^1, η^3-allyl)palladium phosphine complexes react with carbon dioxide and sulphur dioxide by insertion into the palladium-carbon σ-bond to give η^3-allylpalladium-carboxylate and -S-sulphinate complexes.

Bis(η^3-allyl)nickel complexes are known to react with carbon dioxide, in the presence of basic phosphines, to give η^3-allylnickel carboxylates (1)

$$(\eta^3\text{-2-}CH_3C_3H_4)_2Ni + CO_2 \xrightarrow{P(CH_3)_3} \eta^3\text{-2-}CH_3C_3H_4Ni(OCOC_4H_7)P(CH_3)_3$$

Insertion has been suggested to be preceded by conversion of one η^3-allyl group into the η^1-form. Incorporation of CO_2 has also been observed in reactions with (η^3-allyl)$_2$Ni (2) and η^3-allyl-Pd(X)L complexes (3) without, however, isolation of the intermediates involved. Recently we have shown that the adducts formed by bis(η^3-allyl)palladium complexes with basic phosphines contain both η^1- and η^3-allyl groups (4) and we report here their reactions with carbon dioxide and sulphur dioxide.

Carbon dioxide reacts readily at -30° to -20° with a toluene solution of the (η^1, η^3-$C_3H_5)_2PdPR_3$ (R = CH_3,C_6H_{11}) complexes to give η^3-allylpalladium carboxylates (I) as pale yellow solids. The 2-methylallyl complexes react similarly. I absorbs two equivalents of CO at room temperature eliminating 2-propenyl-2-butenoate. Hydrogenation followed by protonolysis liberates butyric acid



Similar reactions are observed with sulphur dioxide at -30° : palladium-S-sulphinate complexes (II) are formed. The formulation of II as an S-sulphinate derivative, rather than the less common O-sulphinate form, is supported by the presence of the diagnostic absorptions in the infrared spectrum (KBr disc) at 1150 and 1025 cm^{-1} (R=CH_3) which are attributed to the asymmetric and symmetric SO_2 stretching frequencies (5) . II also undergoes reductive elimination upon reaction with CO at room temperature to give a 1 : 1 mixture ($R=CH_3$) of diallylsulphone and allyl,2-propenylsulphone.

The structural assignment of I and II is supported by their ^1H- and ^{13}C-nmr spectra. The ^{13}C-nmr spectral data is summarized below.

Complex ($R=C_6H_{11}$)	$\delta C_1 (J_{C,P}; J_{C,H})$	$\delta C_2 (J_{C,P})$	$\delta C_3 (J_{C,P})$	$\delta C_4 (J_{C,H})$	δC_5	δC_6
I [a)]	44.82(1.1;158±2)	116.01(4.3)	79.88(26.9)	44.9(126±5)	138.22	114.78
II	58.59(– ;159±2)	120.88(4.2)	72.33(26.2)	77.10(140±5)[b)]	132.92	119.89

a) δCO 175.7 ppm b) $J_{P,C}$ 2.4 Hz

Characteristic are the large coupling constants for the allylic-carbon atoms <u>trans</u> to phosphorus (J_{P,C_3}) and the difference in $J_{C,H}$ for C_1 (sp^2-hybridized) and C_4 (sp^3-hybridized).

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