

Preliminary Communication

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

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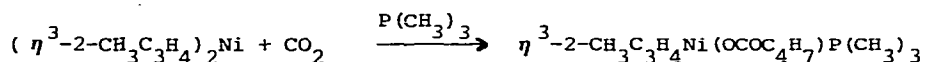
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Summary

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-sulphinates complexes.

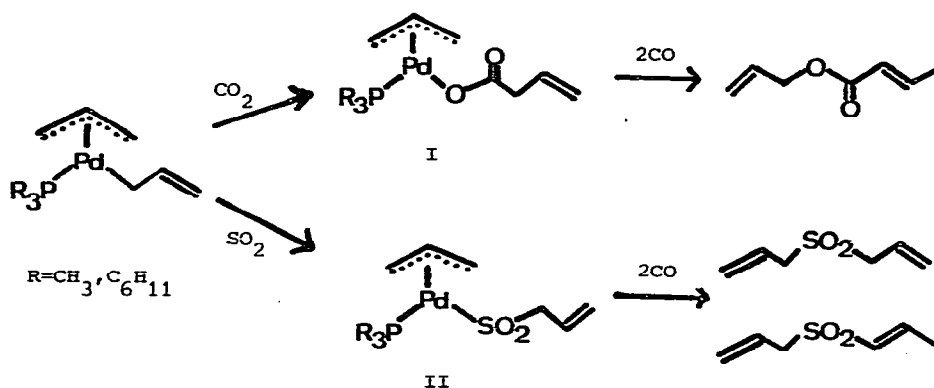
Bis(η^3 -allyl)nickel complexes are known to react with carbon dioxide, in the presence of basic phosphines, to give η^3 -allyl-nickel carboxylates (1)



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 $(\eta^3\text{-allyl})_2\text{Ni}$ (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) $_2$ PdPR $_3$ (R = CH $_3$, C $_6$ H $_{11}$) complexes to give η^3 -allylpalladium carboxylates (I) as pale yellow solids. I absorbs two equivalents of CO at room temperature eliminating 2-propenyl-2-butenolate. 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 diallyl-sulphone 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 trans 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).

References.

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5. See for example G. Vitzthum and E. Lindner, *Angew. Chem.* **83**, 315 (1971)