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CYCLOPALLADATION OF PHOSPHINE IMIDES

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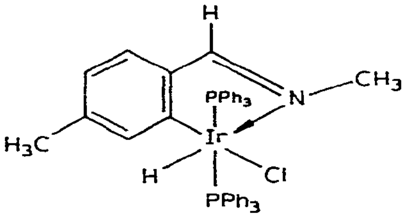
Summary

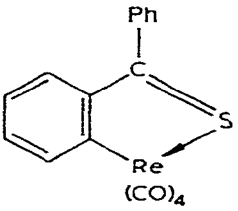
The first examples of transition metal *ortho*-metalated complexes of phosphine imides are described. Reaction of triarylphosphine imides with tetrachloropalladate in methanol affords the cyclometalated complexes in 56—97% yields.

Introduction

A subject of great recent interest is the transition metal intramolecular *ortho*-metalation of organic compounds containing donor ligands such as nitrogen (I) [1] and sulfur (II) [2] *. While many different types of such complexes are known, there have been no reports on the cyclometalation of phosphine imides by transition metals.



(I)



(II)

Several interesting reactions of transition metal compounds with phosphine imides have been described. Deoxygenation of a carbonyl group of iron pentacarbonyl occurred on treatment with triphenylphosphine imides to give isocyanide complexes and triphenylphosphine oxide [4]. A similar deoxygenation takes place when carbon monoxide is treated with triphenylphosphine *N*-phenylimide

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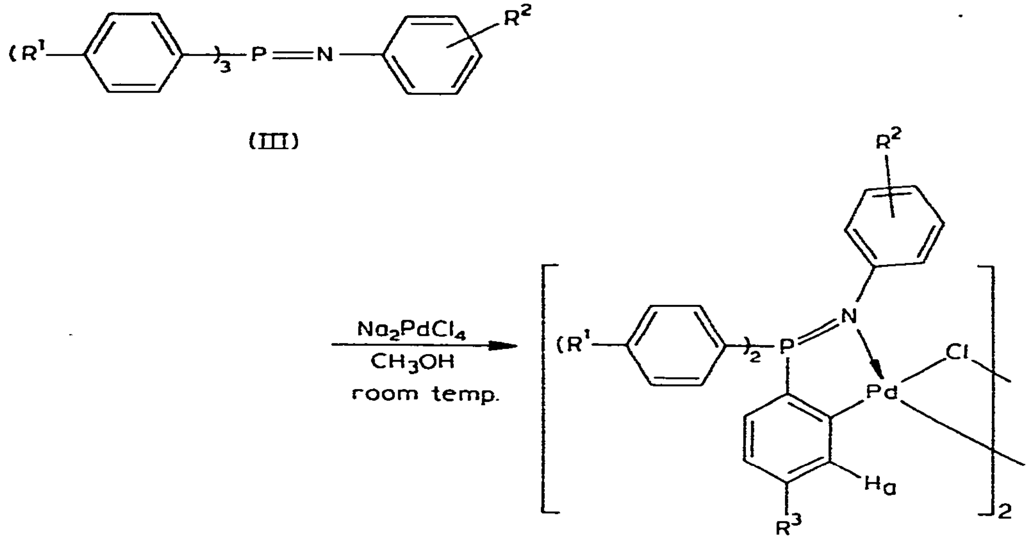
* For a list of types of cyclometalated complexes, see ref. 3.

in the presence of palladium chloride [5]. It seemed conceivable that triarylphosphine imides could undergo cyclization with palladium (and possibly other metals) under appropriate conditions. This paper reports the first examples of cyclometallated complexes of phosphine imides.

Results and discussion

Treatment of a phosphine imide (III, $R^1 = H$, $R^2 = m\text{-}CH_3, p\text{-}CH_3, p\text{-}OCH_3$; $R^1 = CH_3$, $R^2 = p\text{-}OCH_3$) with tetrachloropalladate in methanol at room temperature affords the dimeric five-membered ring cyclopalladated complexes (IV) in 56—97% yields (Table 1). The structures of these compounds were elucidated



(III)

(IV)

TABLE 1

YIELDS, MELTING POINTS AND ANALYTICAL DATA FOR COMPOUNDS IV

R^1	R^2	R^3	Yield (%)	M.p. (°C)	Anal. found (calcd.) (%)		
					C	H	Pd
H	$m\text{-}CH_3$	H	56	168—169	59.66 (59.08)	4.18 (4.16)	20.85 (20.93)
H	$p\text{-}CH_3$	H	97	189—190	59.38 (59.08)	3.96 (4.16)	21.08 (20.93)
H	$p\text{-}OCH_3$	H	76	176—177	56.78 (57.27)	4.33 (4.04)	19.81 (20.29)
CH_3	$p\text{-}OCH_3$	CH_3	61	173—174	59.44 (59.38)	4.76 (4.81)	19.02 (18.79)

TABLE 2

PERTINENT SPECTRAL DATA FOR III AND IV

Compound				IR(CHCl$_3$) (cm^{-1})	NMR [a] (δ, ppm)	Solvent
No.	R^1	R^2	R^3			
III	H	m-CH$_3$		1590, 1566, 1475, 1325	2.12(s, 3H, CH$_3$), 6.33—7.90 (m, 19H, aromatic protons)	CDCl$_3$
IV	H	m-CH$_3$	H	1590, 1568, 1495, 1472, 1165	2.17(s, 3H, CH$_3$), 6.58—7.82 (m, 17H, aromatic) 8.08 (m 1H, H$_a$)	DMSO-d_6
III	H	p-CH$_3$		1602, 1575, 1478, 1323	2.07(s, 3H, CH$_3$), 6.50(d, 2H, protons *ortho* to CH$_3$ bearing carbon, J 8Hz), 6.69(d, 2H, protons *meta* to CH$_3$ bearing carbon), 7.42—7.92 (m, 15H, remaining aromatic protons)	DMSO-d_6
IV [b]	H	p-CH$_3$ [b]	H	1600, 1590, 1490, 1470, 1170	2.11(s, 3H, CH$_3$), 6.57—7.97 (m, 17H, aromatic protons), 8.07 (m, 1H, H$_a$)	DMSO-d_6
III	H	p-OCH$_3$		1596, 1581, 1484, 1322	3.62 (s, 3H, OCH$_3$), 6.58(s(br), 4H, protons on OCH$_3$ substituted ring) 7.17—7.83(m, 15H, aromatic protons)	CDCl$_3$
IV	H	p-OCH$_3$	H	1598, 1588, 1497, 1466, 1163	3.68(s, 3H, OCH$_3$), 6.53—8.05(m, 18H, H$_a$ and other aromatic protons)	CDCl$_3$
III	CH$_3$	p-OCH$_3$		1598, 1576, 1460, 1310	2.35(s, 9H, CH$_3$), 3.63(s, 3H, OCH$_3$), 6.53—7.75(m, 16H, aromatic protons)	CDCl$_3$
IV	CH$_3$	p-OCH$_3$	CH$_3$	1600, 1575, 1495, 1450, 1173	220(s, 3H, R^3 = CH$_3$), 2.40(s, 6H, R^1 = CH$_3$), 3.68(s, 3H, OCH$_3$), 6.38—7.80(m, 14H, aromatic protons), 7.93(d, 1H, H$_a$, J_{meta} 2.0 Hz)	CDCl$_3$

[a] Tetramethylsilane was used as internal standard (δ(TMS) 0). [b] Molecular weight found(osmometry) 998; calcd: 1017.

on the basis of analytical (Table 1), infrared (IR) and nuclear magnetic resonance (NMR) spectral data (Table 2).

The IR spectra of III display an intense P=N stretching band at 1310—1325 cm^{-1} ($CHCl_3$), which disappears on complexation. A strong adsorption at 1163—1173 cm^{-1} in the IR spectra of IV, is assigned to the P=N vibration, the shift due to withdrawal of electron density from nitrogen by palladium. Another difference between the IR spectra of III and IV is the appearance, in the latter, of an extra ν(CC) absorption in the region of 1490—1497 cm^{-1}. This observation is indicative of a change in a phenyl group substitution pattern [6].

The ^{1}H NMR spectrum of IV showed a low field absorption due to the proton *ortho* to the palladium substituted carbon [7]. Further evidence for structure IV was obtained with tri-*p*-tolylphosphine *N*-(*p*-methoxyphenyl)imide ($R^1 = R^3 = CH_3$, $R^2 = p\text{-}OCH_3$). Two methyl signals were observed (δ 2.20, 2.40 ppm) clearly indicating the presence of two different tolyl groups in IV ($R^1 = R^3 = CH_3$, $R^2 = p\text{-}OCH_3$).

Complexes of the type L_2PdCl_2 (L = III) were not isolated from these reactions. Benzoylsulfilimines, containing the S=N linkage, react with Na_2PdCl_4 to form L_2PdCl_2 complexes, where the sulfilimine ligand (L) is coordinated through the nitrogen atom [8]. It should be possible to prepare cyclometalated complexes of sulfilimines, analogous to IV, using appropriately substituted ligands.

Experimental

General

Melting points were determined using a Fisher—Johns apparatus and are uncorrected. Infrared spectra were recorded on a Beckman 1R20A spectrometer, equipped with a calibration standard. Proton NMR spectra were determined on a Varian T60 spectrometer. Elemental analyses were performed by Drs. F. Pascher and E. Pascher, Microanalytical Laboratory, Bonn, West Germany.

Triphenylphosphine *N*-*m*-tolylimide (III, $R^1 = H$, $R^2 = m\text{-}CH_3$) was purchased from Maybridge Chemical Co., and was used as received. Triphenylphosphine *N*-*p*-tolylimide (III, $R^1 = H$, $R^2 = p\text{-}CH_3$, m.p. 132—134°C and triphenylphosphine *N*-(*p*-methoxyphenyl)imide (III), $R^1 = H$, $R^2 = p\text{-}OCH_3$, m.p. 118—119°C) were synthesized according to literature procedures [9]. Tri-p-tolylphosphine *N*-(*p*-methoxyphenyl)imide (III, $R^1 = CH_3$, $R^2 = p\text{-}OCH_3$) was prepared in 85% yield following the general procedure of Horner and Oediger. m.p. 123—125°C. Found: C, 79.11; H, 6.49. $C_{28}H_{28}NOP$ calcd.: C, 79.03; H, 6.63%.

Disodium tetrachloropalladate was purchased from Alfa Inorganics, Inc., and was used as received. All reactions were run under a nitrogen atmosphere.

General procedure for reactions of phosphine imides (III) with Na_2PdCl_4

A methanol solution (15—25 ml) of 1.5 mmol of phosphine imide was slowly added to a methanol (20—23 ml) solution of Na_2PdCl_4 (0.441 g, 1.5 mmol). The mixture was stirred for 2.5—4.0 h at room temperature, during which time precipitation of the cyclopalladated complex IV occurred. The product was filtered, washed well with cold methanol, then ether, and then dried in vacuo. Pertinent physical data for these air-stable complexes are listed in Tables 1 and 2.

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