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CYCLOPENTADIENYL TITANIUM COMPLEXES WITH ARYLDIAZENIDO- OR PHOSPHINIMINATO-LIGANDS

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Summary

[Ti(η^5-C_5H_5)Cl_3] reacts with Me_3Si—N=N—Ph to give [Ti(η^5-C_5H_5)Cl_2(N_2Ph)], and this gives [Ti(η^5-C_5H_5)$_2$Cl(N_2Ph)] on treatment with sodium cyclopentadienide in THF at —80°C. [Ti(η^5-C_5H_4R)Cl_3] (R = H, Me) reacts analogously with Me_3Si—N=PR_3 (PR_3 = PPh_3, PPh_2Me) to give [Ti(η^5-C_5H_4R)Cl_2(NPR_3)]. Under similar conditions $TiCl_4$ gives [$TiCl_4$(Me_3SiNPR_3)].

Although there is an extensive chemistry of both the aryldiazenido- and nitrido-ligands with the heavier transition metals, there are to date no reported examples of well-defined titanium complexes of these ligands. The aryldiazenido-ligand has been implicated in the formation of aromatic amines from [Ti(η^5-C_5H_5)$_2$(η^1-C_6H_5)$_2$] and dinitrogen [1]. Nitrides are believed to be involved in the reductive generation of ammonia from [{Ti(η^5-C_5H_5)$_2$(η^1-C_6H_5)}$_2$(N_2)] [2] and in many other nitrogen fixing systems based on admixtures of titanium species and strong reducing agents [3].

A lack of suitable precursors ruled out phenylhydrazine or phenyldiazonium salts as sources of the aryldiazenido-ligand, and Me_3SiN_2Ph, used to prepare manganese phenyldiazenido-complexes [3], was employed. The blue silyldiazene was prepared by a slight modification of a literature method [4]. [Ti(η^5-C_5H_5)Cl_3] reacted rapidly with Me_3SiN_2Ph in THF at room temperature to give an 80% yield of orange [Ti(η^5-C_5H_5)Cl_2(N_2Ph)] (I) which could be recrystallised from diethyl ether. However [Ti(η^5-C_5H_5)$_2$$Cl_2$] did not react with the silyldiazene even in refluxing toluene, and the green complex [Ti(η^5-C_5H_5)$_2$Cl(N_2Ph)] (II) was prepared in about 60% yield by reaction of I with sodium cyclopentadienide in THF at —80°C. Analytical and spectroscopic data for these complexes are summarized in Table 1. Attempts to prepare the nitrosyl analogue

TABLE 1

TITANIUM PHENYLDIAZENIDO- AND PHOSPHINIMINATO-COMPLEXES

Number	Complex	Analysis Found (calcd.) (%)					^{1}H NMR resonances[a]		IR	Mol. wt.[b]
		C	H	N	Ti	Cl	Observed	Assignment		
I	[Ti(η^5-C_5H_5)Cl_2(N_2Ph)]	45.4	3.6		16.6	24.7	6.50s	C_5H_5 protons	1593[c]	298
		(45.6)	(3.5)		(16.6)	(24.5)	7.6m, 8.2m	phenyl protons		(289)
II	[Ti(η^5-C_5H_5)$_2$Cl(N_2Ph)]	60.3	5.4		14.8	11.3	5.87s	C_5H_5 protons	1632[c]	305
		(60.4)	(4.7)		(15.1)	(11.2)	7.5m	phenyl protons		(318)
III	[Ti(η^5-C_5H_5)Cl_2(NPPh_3)]	60.1	4.6	2.9	9.9	14.9			1150[d]	
		(60.0)	(4.3)	(3.0)	(10.4)	(15.4)				
IV	[Ti(η^5-C_5H_5)Cl_2(NPPh_2Me)]	53.8	4.6	3.4	11.2				1150[d]	
		(54.3)	(4.5)	(3.5)	(12.0)					
V	[Ti(η^5-C_5H_4Me)Cl_2(NPPh_3)]	60.8	4.9	2.8					1150[d]	
		(60.8)	(4.6)	(3.0)						
VI	[TiCl_4(Me_3SiNPPh_3)]	47.0	4.9	2.3	9.0	26.2			975[d]	
		(46.6)	(4.4)	(2.6)	(8.9)	(26.2)				

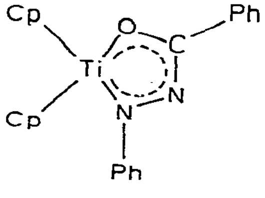
[a] In CS_2 solution. [b] Calculated values in parentheses. [c] $\nu(N{=}N)$. [d] $\nu(P{=}N)$.

of I by reaction of $[Ti(\eta^5\text{-}C_5H_5)Cl_2]$ with a stoichiometric amount of NO at —80°C caused immediate liberation of dinitrogen and formation of titanium oxo species, as evidenced by strong IR bands in the 700—800 cm^{-1} region.

The ^1H NMR spectra of the complexes showed singlets at about 6 ppm due to cyclopentadienyl protons and multiplets in the 7—8 ppm region due to the diazenide-aryl protons. Medium intensity IR bands at 1593 (I) and 1632 (II) cm^{-1} were assigned to $\nu(N{=}N)$ of the diazenido-ligand. The mass spectra showed peaks due to the mass ions, and the spectrum of I showed a number of peaks attributable to dimeric products, although the complex is monomeric in benzene solution. The peak at *m/e* 436 is assigned to the dimeric ion formed by the elimination of $C_6H_5N_2Cl$ between two molecules of I. The spectrum of II shows a peak attributable to $[Ti(\eta^5\text{-}C_5H_5)_2Cl(\eta^1\text{-}C_6H_5)]$ formed by extrusion of N_2 from the phenyldiazenido-ligand.

Complex II reacted instantaneously with HCl in diethyl ether to give $[Ti(\eta^5\text{-}C_5H_5)_2Cl_2]$ and unidentified organic fragments. With HBF_4 in diethyl ether orange-red products were produced, which decomposed on attempted purification. The reactions of complex II with Grignard and lithium reagents to give the derivatives $[Ti(\eta^5\text{-}C_5H_5)_2R(N_2Ph)]$ will be discussed elsewhere.

Attempts to benzoylate the diazenido-ligand by reaction with benzoyl chloride failed, and no reaction occurred in diethyl ether at room temperature after 16 h. However the 1-phenyl-2-benzoyldiazene complex $[Ti(\eta^5\text{-}C_5H_5)_2(PhCON_2Ph)]$ was prepared by reaction of the dilithium salt of PhCONHNHNPh with $[Ti(\eta^5\text{-}C_5H_5)_2Cl_2]$ in diethyl ether as solvent. The brown crystalline complex showed no IR bands assignable to $\nu(N{=}N)$ or $\nu(C{=}O)$ suggesting the same chelated delocalised structure (A) found in the complexes $[MoCl_2(NPh)(PhCON_2Ph)(PMe_2Ph)]$ [5] and $[OsCl_2(PhCON_2Ph)(PPh_3)_2]$ [6].



(A)

Phosphiniminato-complexes of osmium can be prepared by reaction of nitrido-complexes with tertiary phosphines, and can be oxidised to nitrido-complexes [7]. We here report the preparation of some titanium phosphiniminato-complexes as potential precursors for titanium nitrido-complexes and derivatives with titanium-nitrogen bonds. The silyl phosphinimine $Me_3Si{-}N{=}PPh_3$ reacts smoothly with $[Ti(\eta^5\text{-}C_5H_4R)Cl_3]$ (R = H, Me) in diethyl ether at room temperature to give the bright yellow crystalline phosphiniminato-complexes $[Ti(\eta^5\text{-}C_5H_4R)Cl_2(NPPh_3)]$ (III—V). As before, $[Ti(\eta\text{-}C_5H_5)_2Cl_2]$ did not react with the silylphosphinimine even in refluxing toluene, and brown uncharacterisable products were obtained from its reaction with $Ph_3P{=}NLi$ in THF. Attempts to use other titanium precursors such as $[TiCl_3(THF)_3]$ were unsuccessful, but $TiCl_4$ in diethyl ether reacted with $Me_3SiNPPh_3$ to give $[TiCl_4(Me_3SiNPPh_3)]$ (VI). The phosphiniminato-complexes III to V show strong broad IR bands at

1150 cm^{-1} assigned to ν(P=N) [5], whereas VI has a strong band at 975 cm^{-1} attributed to ν(P=N) and other bands at 1250 and 650 cm^{-1} due to the Me_3Si group. The lowering of ν(P=N) in complex VI from the free ligand value of 1112 cm^{-1} is consistent with N-bonding of the ligand.

Lack of solubility precluded ^{1}H NMR or molecular weight determination of the phosphiniminato-complexes and complex VI decomposed on solution in THF. The mass spectra of complexes III—V show *m/e* peaks due to the mass ions, and the most intense peaks are assigned to the ions $[TiCl_2(NPPh_3)]^+$, formed by loss of a C_5H_5 group.

Experimental

The following compounds were prepared by literature procedures: $[Ti(\eta^5\text{-}C_5H_5)Cl_3]$ [8], $[Ti(\eta^5\text{-}C_5H_4Me)Cl_3]$ [8], $[Ti(\eta^5\text{-}C_5H_5)_2Cl_2]$ [9], $Me_3Si—N{=}PPh_3$ [10] and $Me_3Si—N{=}PPh_2Me$ [10]. All reactions were carried out in conventional Schlenk glassware under dry, deoxygenated nitrogen, using solvents dried by normal procedures.

The IR spectra were recorded as Nujol mulls using a JASCO IRA-2 spectrophotometer and ^{1}H NMR spectra in appropriate solvents using a Jeol 60 HL instrument. Mass spectra were recorded by Mr. A. Kiewiet of the University of Groningen, using an AEI-MS 9 instrument. Elemental analysis were carried out by Mr. A.F. Hamminga at the University of Groningen and Mr. P.E. Meadows at the University of Sussex.

1-Trimethylsilyl-2-phenylhydrazine

Trimethylsilyl chloride (75 ml) in diethyl ether (50 ml) was added dropwise over 2 h to a rapidly stirred solution of phenylhydrazine (54 ml) and triethylamine (89 ml) in diethyl ether (800 ml). The resulting white suspension was then heated to reflux for 16 h, cooled and filtered, the precipitate of triethylamine hydrochloride being washed thoroughly with diethyl ether (2 × 100 ml). The diethyl ether was removed by distillation at atmospheric pressure and the residue distilled at 82—84°C and 2 mmHg (yield 79 g, 88%).

1-Trimethylsilyl-2-phenyldiazene

1-Trimethylsilyl-2-phenylhydrazine (35 ml) and di-t-butyl peroxide (35 ml) were heated to 200°C under nitrogen under a 30 cm Vigreux column equipped with a variable reflux ratio take-off. Heating was continued until no more t-butanol (b.p. 85°C) distilled over and the bright blue residue was then fractionally distilled at 2 mmHg and the fraction boiling at 92—96°C collected. (Yield 12.3 g, 35%).

Dichlorocyclopentadienyl{phenyldiazenido(1—)}titanium(IV) (I)

1-Trimethylsilyl-2-phenyldiazene (1.8 g, 9.5 × 10^{-3} mol) was added dropwise with stirring at —10°C to a solution of cyclopentadienyltrichlorotitanium(IV) (2.0 g, 9.1 × 10^{-3} mol) in tetrahydrofuran (30 ml). The resulting orange-brown solution was stirred at room temperature for 1 h and evaporated to a sticky oil, which was then triturated with cold diethyl ether (20 ml) to give the complex as an orange-brown powder. This was washed with a further portion of cold diethyl ether (15 ml) and was sufficiently pure for subsequent reactions (yield 1.9 g, 72%). Analytically pure samples were recrystallised from diethyl ether at —40°C.

Chlorodicyclopentadienyl{phenyldiazenido(1—)}titanium(IV) (II)

A solution of sodium cyclopentadienide (5.3 ml of a 0.037 g/ml solution) was added dropwise with stirring at —80°C to a solution of complex I (0.66 g) in tetrahydrofuran (40 ml). The pale green suspension was allowed to warm to room temperature and evaporated to a dark green solid which was extracted with diethyl ether (2 × 30 ml). On cooling the ethereal extracts to —60°C the complex crystallised out as pale green needles which were washed with diethyl ether at —80°C (yield, 0.42 g, 58%).

The same complex was obtained in rather lower yield (25%) using half an equivalent of dicyclopentadienylmagnesium.

N-Benzoyl-N'-phenyldiazene-(N',O)dicyclopentadienyltitanium(II)

N-Benzoyl-*N'*-phenylhydrazine (0.5 g) in diethyl ether (40 ml) was treated dropwise with n-butyllithium (2.5 ml of 2 *N* solution in hexane) to give a pale yellow precipitate of the dilithium salt of the hydrazine. Powdered dichlorodicyclopentadienyltitanium(IV) was added and the reaction mixture stirred at room temperature for 1 h and then filtered. The resulting brown filtrate was evaporated in vacuo to 20 ml and allowed to stand at —30°C for 24 h to give brown prisms of the complex. Analysis: Found: C, 70.7; H, 5.4; N, 7.1; Ti, 12.3. $C_{23}H_{20}N_2Cl_2Ti$ calcd.: C, 71.1; H, 5.2; N, 7.2; Ti, 12.3%.

Dichlorocyclopentadienyl{triphenylphosphiniminato(1—)}titanium(IV) (IV)

A solution of trimethylsilylphosphinimine (1.4 g, 4.0×10^{-3} mol) in diethyl ether (25 ml) was added dropwise with stirring at room temperature to a solution of trichlorocyclopentadienyltitanium (0.84 g, 3.8×10^{-3} mol) in diethyl ether (40 ml). After stirring for 1 h, the complex had precipitated as a bright yellow microcrystalline solid, which was washed with diethyl ether at 0°C (20 ml). (Yield 1.4 g, 70%). The complex was recrystallised as chunky yellow prisms from toluene at —30°C.

Complexes V and VI were prepared similarly using the appropriate titanium complex and trimethylsilylphosphinimine.

Tetrachloro(trimethylsilylphosphinimine)titanium(IV) (VII)

A solution of trimethylsilylphosphinimine (0.79 g, 2.2×10^{-3} mol) in diethyl ether (25 ml) was added to a solution of titanium tetrachloride (0.42 g, 2.2×10^{-3} mol) in diethyl ether (30 ml) with stirring at room temperature. After 1 h the complex precipitated as a yellow microcrystalline solid which was washed with diethyl ether (20 ml). (Yield 0.96 g, 79%).

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