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INTERACTION OF 1,3-DIARYLTRIAZENIDO-TRIMETHYLSILICONS AND -TRIMETHYLTINS WITH CARBONYL HALIDES OF MANGANESE, MOLYBDENUM AND RHODIUM

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Summary

The 1,3-diaryltriazenido-trimethylsilicons and -trimethyltins underwent reaction with bromopentacarbonylmanganese, chlorotricarbonyl-η^5-cyclopentadienylmolybdenum, and bis(chlorodicarbonylrhodium) to give rapid, high yield syntheses of the corresponding 1,3-diaryltriazenido derivatives of the transition metals. The complexes of molybdenum and manganese were monomeric with chelating triazenido groups, but the rhodium complexes were dimeric with bridging triazenido groups.

In the $R_2N_3Mn(CO)_4$ complexes, phosphines and arsines replaced carbon monoxide rather than the triazenido groups, at the metal centre.

Introduction

A wide range of organonitrogen derivatives of silicon and tin have been shown to be excellent reagents for the synthesis of organonitrogen transition metal complexes [1].

The 1,3-diaryltriazenido-trimethylsilicons [2] and -trimethyltins [3,4] may be prepared in high yields and can be stored indefinitely, and are therefore potentially useful as off-the-shelf precursors for the synthesis of transition metal complexes containing the triazenido ligand.

In addition to the early work of Dwyer [5] and that of others [6—9] upon the metal complexes of the triazenido ion, a number of organometallic and metal carbonyl triazenido complexes have been reported [10,11].

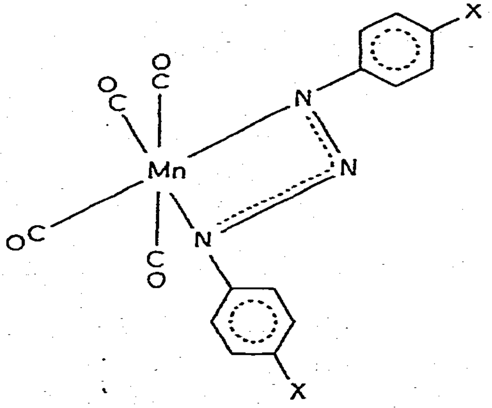
Results and discussion

The diaryltriazenidotrimethyltins undergo reaction with bromopentacarbonylmanganese according to eq. 1.

$$(p\text{-}XC_6H_4)_2N_3SnMe_3 + Mn(CO)_5Br \rightarrow (p\text{-}XC_6H_4)_2N_3Mn(CO)_4 + Me_3SnBr + CO \quad (1)$$

$(X = H, Cl, Me)$

These 1,3-diaryltriazenidotetracarbonyls of manganese are all orange air stable crystalline solids produced in ~80% yield. On the basis of IR spectra King [11] has proposed for the diphenyl complex, the structure illustrated (I). We have obtained the same four active modes in the carbonyl stretching region of the IR spectrum, though in the case of the p-Cl derivative the four bands were at markedly higher frequencies. We have now demonstrated the monomeric nature of these complexes by solution molecular weight measurements and mass spectrometry.



(I)

In the ^{1}H NMR spectrum of 1,3-di(p-tolyl)triazenidotetracarbonyl there is only one sharp CH_3 signal indicating the equivalence of environment of the two methyl groups; further the ^{1}H NMR signal in the aromatic region of the p-tolyl and p-chlorophenyl complexes are only interpretable in terms of a single four spin configuration of C_{2v} symmetry. This exact equivalence of the two aromatic rings in these monomers confirms the highly symmetrical structure I.

The mechanism of formation of these complexes probably involves initial displacement of carbon monoxide by the organotin triazine, followed by an intramolecular elimination of bromotrimethyltin; as previously proposed for comparable systems [1].

The diaryltriazenidotrimethylsilicons gave analogous reactions to those represented in eq. 1, with the same mild conditions and high yields.

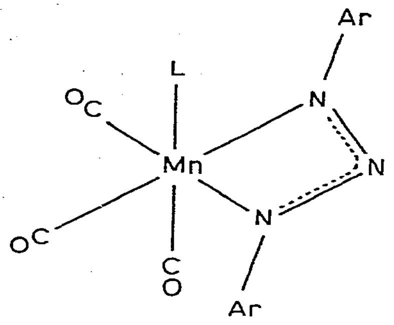
The 1,3-diaryltriazenidotetracarbonyls of manganese underwent reaction with phosphine and arsine ligands according to eq. 2.

$$(p\text{-}XC_6H_4)_2N_3Mn(CO)_4 + L \rightarrow (p\text{-}XC_6H_4)_2N_3Mn(CO)_3L + CO \quad (2)$$

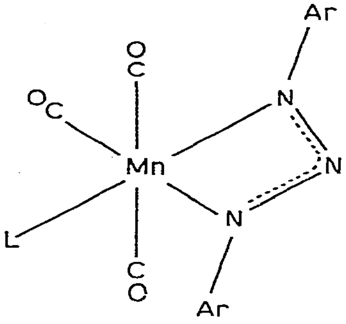
$(X = CH_3 \text{ and } Cl; L = Ph_3P, Me_2PhP \text{ and } Ph_3As)$

One carbonyl group was displaced, with no indication of further incorporation of phosphine or arsine. An alternative possible reaction would involve the phosphine or arsine displacing a nitrogen of the triazenido ligand, whence it would become a monodentate one electron donor in place of a pseudo-allyl formally three electron donor. No trace of this alternative was noted.

Of the two possible structures for these phosphine and arsine substituted complexes (II and III), we would favour the *fac* form (II). The three observed CO stretching modes in these complexes are of approximately equal intensity which indicates [12] that they are the $2A' + A''$ modes of the *fac* isomer (II), rather than the $2A_1 + B_1$ modes of the *mer* isomer (III).



(II)



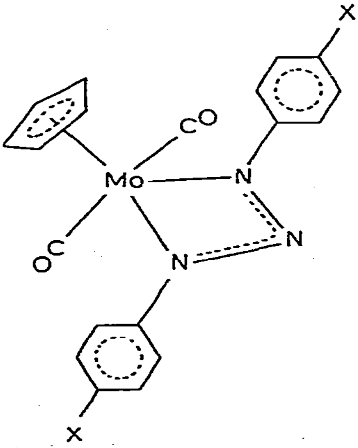
(III)

The interaction of chlorotricarbonyl-η^5-cyclopentadienylmolybdenum and the diaryltriazenidotrimethyltins produce the 1,3-diaryltriazenidodicarbonyls of molybdenum according to eq. 3.

$$(p\text{-}XC_6H_4)_2N_3SnMe_3 + (\eta^5\text{-}C_5H_5)Mo(CO)_3Cl \rightarrow (p\text{-}XC_6H_4)N_3Mo(CO)_2(\eta^5\text{-}C_5H_5) + Me_3SnCl + CO \quad (3)$$

($X = CH_3$ and Cl)

For the corresponding phenyl complex the symmetrical monomeric structure (IV), (X = H) was proposed [11]. The monomeric nature of this class of compounds is confirmed by solution molecular weight determination and by mass spectrometry.



(IV)

The symmetrical nature of the bonding of the triazenido ligands and the overall C_{2v} symmetry of the molecules is demonstrated from their ^1H NMR spectra by the single CH_3 resonance in the *p*-tolyl compound and the two identical aryl rings in the *p*-tolyl and *p*-chloro compounds.

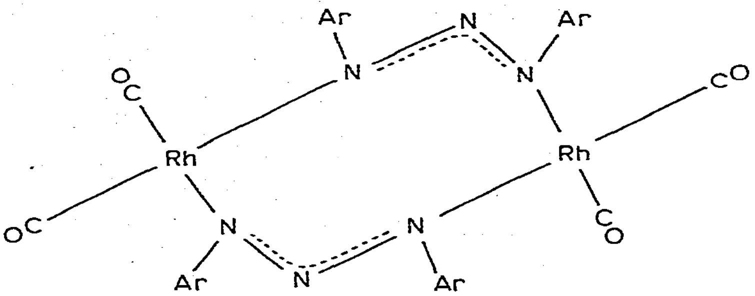
Dicarbonylrhodium complexes of allyl and pseudo-allyl ligands are known which are mononuclear with a chelating (pseudo-allyl) group present [13], and are also known [14] where the pseudo-allyl groups act as bridges in binuclear complexes. Knoth [10] has reported the remarkable reactions where the monomeric cyclo-octadiene complex $(C_8H_8)RhN_3Ph_2$ upon treatment with carbon monoxide has cyclo-octadiene replaced by carbon monoxide, but simultaneously dimerizes to produce $[\{(CO)_2RhN_3Ph_2\}_2]$; yet the complex $(Ph_3P)_2RhN_3Ph_2$ reacted with carbon monoxide to produce the five coordinate monomer $(Ph_3P)_2Rh(CO)N_3Ph_2$.

We were especially interested to observe the nature of the product from the reaction between bis(chlordicarbonylrhodium) and the diaryltrizenidotrimethyltins. This occurred according to eq. (4).

$$2(p\text{-}XC_6H_4)N_3SnMe_3 + \{Rh(CO)_2Cl\}_2 \rightarrow [\{(p\text{-}XC_6H_4)_2N_3Rh(CO)_2\}_2] + 2\ Me_3SnCl \qquad (4)$$

(X = H and CH_3)

The dimeric nature of the product was deduced from solution molecular weight measurements and mass spectra.



(V)

In the light of Knoth's isolation of a five coordinate rhodium triazine complex [10], it is possible that reaction (4) proceeds by the coordination of diaryltriazenidotrimethyltin molecules onto the vacant sites in the rhodium atoms of bis(chlordicarbonylrhodium) followed by two intramolecular eliminations of chlorotrimethyltin. The proposed structure V for the *p*-tolyl complex is confirmed by the presence of only one sharp singlet for the ^1H NMR resonance of the four CH_3 groups in the molecule, and the identical environments of the four aryl rings.

Experimental

All reactions were carried out routinely under an atmosphere of dry nitrogen, and solvents were distilled from potassium benzophenone. IR spectra were recorded in hexane using calcium fluoride 0.1 mm solution cells on a Perkin—Elmer 257 spectrophotometer; ^1H NMR spectra were recorded on a Perkin—

Elmer Hitachi RMU-6 spectrometer, and molecular weights were determined in either benzene or chloroform using a Knauer vapour pressure osmometer.

$Mn(CO)_5Br$ [15], $(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl$ [16], $\{Rh(CO)_2Cl\}_2$ [17], Ar—N=N—N(H)—Ar [18] and Me_3SnNEt_2 [19] were prepared by literature methods.

1-Trimethylsilyl-1,3-diphenyltriazene

To a stirred solution of 1,3-diphenyltriazine (5 g, 25 mmol) in diethylether (10 cc) was added sodium hydride (0.61 g, 25 mmol). After hydrogen liberation had ceased the solution of sodium 1,3-diphenyltriazenide was heated under reflux (1 h). To the warm solution was then added chlorotrimethylsilane (2.75 g, 25 mmol) in diethylether (10 cc). After stirring (8 h) the mixture was heated under reflux (1 h). Sodium chloride was allowed to settle and the solution decanted into a dry flask. Solvent was removed under reduced pressure (30°C/10 mmHg), and the remaining yellow liquid subjected to molecular distillation to give the product (80% yield).

1-Trimethylsilyl-1,3-di(*p*-tolyl)triazene and 1-trimethylsilyl-1,3-di(*p*-chlorophenyl)triazene were prepared in ~75% yields in similar manner to the above.

Interaction of 1-trimethylsilyl-1,3-diphenyltriazene and bromopentacarbonylmanganese

To a stirred suspension of the carbonyl (0.33 g, 1.2 mmol) in hexane (15 cc) at 55°C was added the triazene (0.33 g, 1.2 mmol). Solvent was removed (20°C/15 mmHg) after 2 h, and the resultant yellow solid pumped (20°/0.01 mmHg) 1 h to remove the last traces of bromotrimethylsilane. The residue was crystallized from hexane to give 1,3-diphenyltriazenidotetracarbonylmanganese (0.35 g, 80%) as an orange yellow solid (Table 1) (Molecular weight; found, 359; calculated, 363). Mass spectrum (10 most intense peaks) *m/e* 363, $[Ph_2N_3Mn(CO)_4]^+$ $[M]^+$; 307, $[M-2\ CO]^+$; 279, $[M-3\ CO]^+$; 251, $[M-4\ CO]^+$; 196, $[Ph_2N_3]^+$; 168, $[Ph_2N]^+$; 105, $[PhN_2]^+$; 91, $[PhN]^+$; 77, $[Ph]^+$; 55, $[Mn]^+$.

Interaction of 1,3-diphenyltriazenidotrimethyltin and bromopentacarbonylmanganese

The reaction was carried out in a similar manner to that above, to produce the 1,3-diphenyltriazenidotetracarbonylmanganese (0.37 g, 85%).

Bromopentacarbonylmanganese reacted similarly with 1,3-di(*p*-chlorophenyl)-triazene and 1,3-di(*p*-tolyl)triazene to produce respectively, 1,3-di(*p*-chlorophenyl) triazenidotetracarbonylmanganese (75% yield), (Molecular weight; found, 422; calculated, 432), and 1,3-di(*p*-tolyl)triazenidotetracarbonylmanganese (77% yield), (Molecular weight; found, 395, calculated, 391) (Table 1).

Interaction of 1,3-di(p-tolyl)triazenidotetracarbonylmanganese and triphenylphosphine

To a stirred solution of 1,3-di(*p*-tolyl)triazenidotetracarbonylmanganese (0.2 g, 0.5 mmol.) in hexane (15 cc) at 70°C was added triphenylphosphine (0.13 g, 0.5 mmol). Solvent was removed (20°C/15 mmHg) after 5 h to leave a yellow solid. This was recrystallized from hexane/dichloromethane (40 : 60) to give,

TABLE 1

CHARACTERIZATION OF SOME ORGANOMETALLIC 1,3-DIARYLTRIAZENIDO COMPLEXES OF MANGANESE, MOLYBDENUM AND RHODIUM

Compound	Found (calcd.) (%)			ν(CO) (cm^{-1})	^{1}H NMR (δ, ppm) [a] (recorded in CCl_4)
	C	H	H		
$Ph_2N_3Mn(CO)_4$	52.87	2.62	11.30	2105(8), 2029(10), 2007(6.3), 1965(8.5)	7.8—7.00(m) Ph
	(52.91)	(2.78)	(11.57)		
(p-$MeC_6H_4)_2N_3Mn(CO)_4$	55.61	3.67	10.78	2105(8), 2029(10), 2007(6.3), 1965(8.5)	7.00(s) (C_6H_4); 2.28(s) Me
	(55.26)	(3.61)	(10.74)		
(p-$ClC_6H_4)_2N_5Mn(CO)_4$	44.18	1.84	9.26	2109(8) 2035(10), 2013(6.6), 1971(9)	7.10(qu) (C_6H_4)
	(44.47)	(1.87)	(9.72)		
(p-$NeC_6H_4)_2N_3Mn(CO)_3(PPh_3)$	67.23	4.61	6.71	2035(10), 1957(9), 1921(6)	7.32—6.60(m) (Ar); 2.21(s) Me
	(67.20)	(4.67)	(6.72)		
(p-$MeC_6H_4)_2N_3Mn(CO)_3(AsPh_3)$	62.97	4.20	6.21	2035(10), 1955(9), 1923(6.5)	7.44—6.80(s) (C_6H_4); 2.34(s) (Me)
	(62.79)	(4.36)	(6.28)		2.34(s)
(p-$Cl\ C_6H_4)_2N_3Mn(CO)_3(Me_2PPh)$	51.33	3.74	7.47	2039(10), 1957(9), 1919(7)	7.30—6.70(m) (Ar); 1.64(d) M
	(50.95)	(3.53)	(7.75)		(Me), J(H—P) = 8 Hz
$Ph_2N_4Mo(CO)_2(\eta^5$-$C_5H_5)$	55.05	3.56	10.14	1981(10), 1906(7)	7.4—7.00(m) (Ph); 5.67(s)
	(55.21)	(3.63)	(10.17)		(η^5-C_5H_5)
(p-$MeC_6H_4)_2N_3Mo(CO)_2(\eta^5$-$C_5H_5)$	56.81	4.20	9.20	1981(10), 1907(8)	6.88(s) (C_6H_4); 5.55(s) (η
	(57.14)	(4.31)	(9.52)		(η^5-C_5H_5); 2.25(s) (2 Me's)
(p-$ClC_6H_4)_2N_3Mo(CO)_2(\eta^5$-$C_5H_5)$	46.90	2.65	8.36	1985(10), 1909(6)	7.24—6.85(qu) (C_6H_4);
	(47.30)	(2.70)	(8.71)		5.56(s) (η^5-C_5H_5)
$[Ph_2N_3Rh(CO)_2]_2$	47.21	2.65	12.01	2086(10), 2058(5.3) 2022(10)	7.70—7.00(m) (Ph)
	(47.35)	(2.82)	(11.83)		
$[(p$-$MeC_6H_4)_2N_3Rh(CO)_2]_2$	50.07	3.88	10.41	2085(10), 2057(5.3) 2022(9)	7.10(qu) (C_6H_4); 2.22(s) (Me)
	(50.13)	(3.65)	(10.96)		

[a] (s) = singlet, (d) = doublet, (qu) = quartet, (m) = multiplet. For symmetrical resonances the central point is quoted.

1,3-di(*p*-tolyl)trazenidotricarbonyltriphenylphosphinemanganese (0.27 g, 85%) (Table 1).

In a similar manner were prepared 1,3-di(*p*-di(*p*-chlorophenyl)triazenidotricarbonyldimethylphenylphosphinemanganese (80% yield) and 1,3-di(*p*-tolyl)-triazenidotricarbonyltriphenylarsinemanganese (80% yield) (Table 1).

Interaction of chlorotricarbonyl-η^5-cyclopentadienylmolybdenum and 1,3-diphenyltriazenidotrimethyltin

To a stirred suspension of the carbonyl (0.5 g, 1.78 mmol) in hexane (15 cc) at 55°C was added the triazene (0.64 g, 1.78 mmol). Solvent was removed (20°C/0.01 mmHg/2 h) to remove all chlorotrimethyltin. The residue was dissolved in benzene and filtered through kieselguhr before being chromatographed on basic alumina using a 30 × 2.5 cm column, eluting with benzene. The red band was collected, and solvent removed (50°C/15 mmHg). The residue was crystallized from hexane/dichloromethane (60 : 40) to give 1,3-diphenyltriazenidodicarbonyl-η^5-cyclopentadienylmolybdenum (0.14 g, 20%) as a red crystalline solid (Molecular weight: found, 415; calculated, 413). Mass spectrum (6 most intense peaks) *m/e* 413, $[\eta^5\text{-}C_5H_5Mo(CO)_2N_3Ph_2]^+$ $[M]^+$; 385, $[M - CO]^+$; 357, $[M - 2\ CO]^+$; 329, $[\eta^5\text{-}C_5H_5MoNPh_2]^+$; 252, $[\eta\text{-}C_5H_5MoNPh]^+$; 77, $[Ph]^+$.

In a similar manner were prepared 1,3-di(*p*-chlorophenyl) triazenidodicarbonyl-η^5-cyclopentadienylmolybdenum (22%) (Molecular weight; found, 477; calculated, 482), and 1,3-di(*p*-tolyl)triazenidodicarbonyl-η^5-cyclopentadienylmolybdenum (25%) (Molecular weight, found, 440; calculated, 441). (Table 1).

Interaction of bis(chlorodicarbonylrhodium) and 1,3-diphenyltriazenetrimethyltin

To a stirred suspension of the carbonyl (0.15 g, 0.38 mmol) in hexane (15 cc) at 30°C was added the triazene (0.38 g, 0.77 mmol). Solvent was removed (20°C/15 mmHg) after 15 min, and the resultant dark red solid pumped (20°C/0.01 mmHg/2 h) to remove the last traces of chlorotrimethyltin. The residue was crystallised from hexane to produce bis(1,3-diphenyltriazenidodicarbonylrhodium) (0.16 g, 60%) as a red crystalline solid. (Molecular weight; found, 706; calculated, 710). (Table 1).

Mass Spectrum (8 most intense peaks) *m/e* 710, $[\{(CO)_2RhN_3Ph_2\}_2]^+$; 682; $[M - CO]^+$; 626, $[M - 2\ CO]^+$; 598, $[M - 4\ CO]^+$; 521, $[Rh_2N_6Ph_3]^+$; 105, $[PhN_2]^+$; 103, $[Rh]^+$; 77 $[Ph]^+$ (Table 1).

In a similar manner bis(1,3-di-*p*-tolyl-triazenidicarbonylrhodium) was prepared (60% yield). (Molecular weight: found, 745; calculated, 738). (Table 1).

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