A Novel Dinuclear Tetracarbonyl Complex Containing a Bridging Alkyldiazenido Ligand $[WCl(CO)_2(PMe_2Ph)_2(N{=}NCMe_2CMe_2N{=}N)WCl(CO)_2(PMe_2Ph)_2]$ Formed *via* a Cationic Carbonyldiazoalkane Complex $[WCl(CO)(NN{=}CMe_2)(PMe_2Ph)_3][ZnCl_3(thf)]$†

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Treatment of a diazoalkane complex *mer*-$[WCl_2(NN{=}CMe_2)(PMe_2Ph)_3]$ with CO in the presence of $ZnCl_2$(dioxane) affords a cationic carbonyldiazoalkane complex $[WCl(CO)(NN{=}CMe_2)(PMe_2Ph)_3]$ $[ZnCl_3(thf)]$ (thf = tetrahydrofuran), in which the carbon–carbon coupling of the diazoalkane ligand occurs by reduction with Mg under CO to give a dinuclear tetracarbonyldiazenido complex $[WCl(CO)_2(PMe_2Ph)_2(N{=}NCMe_2CMe_2N{=}N)WCl(CO)_2(PMe_2Ph)_2]$.

Our previous study has shown that diazoalkane complexes such as $[MX_2(NN{=}CRR')(PMe_2Ph)_3]$ and $[MF(NN{=}CRR')(dppe)_2]BF_4$ (M = Mo, W; dppe = $Ph_2PCH_2CH_2PPh_2$; R, R' = H, alkyl or aryl) are readily derived from the dinitrogen complexes *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ and *trans*-$[M(N_2)_2(dppe)_2]$, respectively, by the initial protonation of the coordinated dinitrogen with inorganic acids and the subsequent condensation of the resulting hydrazido(2−) ligand with aldehydes or ketones.[2–4] This reaction presents a very versatile method to prepare the organonitrogen ligands from molecular nitrogen, but investigation of the reactivities of

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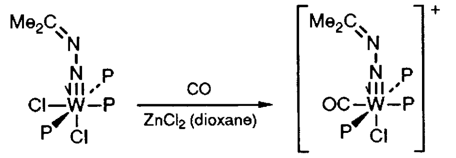
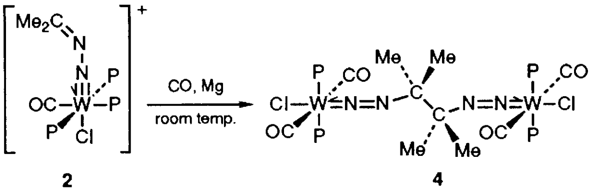
† For Part 35 of the Series, see ref. 1.



1 **2** (1)



2 **4** (2)

P = PMe$_2$Ph

these diazoalkane complexes is still limited. Very recently, we have reported that treatment of the diazoalkane complexes *mer*-[MCl$_2$(NN=CRR')(PMe$_2$Ph)$_3$] with a variety of π-acceptor substrates in toluene at 50 °C gives new diazoalkane complexes [MCl$_2$(L)(NN=CRR')(PMe$_2$Ph)$_2$] (L = alkenes, CO, isonitrile or aldehydes), in which the π-acceptor substrates bind to the metal *cis* to the diazoalkane ligand, concurrent with dissociation of one PMe$_2$Ph ligand.[1]

Now we have found that the reaction of *mer*-[WCl$_2$(NN=CMe$_2$)(PMe$_2$Ph)$_3$] **1** with CO in toluene at room temperature in the presence of ZnCl$_2$ (dioxane) results in the formation of a cationic diazoalkane complex with a CO ligand *mer*-[WCl(CO)(NN=CMe$_2$)(PMe$_2$Ph)$_3$] [ZnCl$_3$(thf)] **2**, which was isolated as red crystals in 73% yield after recrystallizing the product from thf–hexane [eqn. (1)]. The IR spectrum of **2** shows a characteristic ν(CO) band at 1990 cm^{-1} and a ν(C=N) band at 1582 cm^{-1}, whereas the ^{1}H and ^{31}P NMR spectra are diagnostic of the *mer*-configuration of three PMe$_2$Ph ligands in an octahedral pattern.‡ Since the π-back donation from the metal in **2** presumably occurs most effectively to the *cis* direction with respect to the diazoalkane ligand as already observed for other d^2 W^{IV} complexes,[1,5–7] it is plausible that the CO ligand occupies the position *cis* to the diazoalkane ligand and *trans* to the PMe$_2$Ph ligand.

The cyclic voltammetry of the cationic diazoalkane complex **2** in CH$_2$Cl$_2$–Bu$^n_4$NBF$_4$ (0.1 mol dm^{-3}) shows that an irreversible one-electron reduction occurs at −1.8 V *vs.* SCE (SCE = saturated calomel electrode). In contrast, the neutral diazoalkane complexes **1**[4] and [WCl$_2$(CO)(NN=CMe$_2$)(PMe$_2$Ph)$_2$] **3**[1] reported in the previous papers exhibit no reduction wave in its cyclic voltammogram recorded analogously. This finding prompted us to investigate in detail the product generated from **2** under reductive conditions. Since the LUMO in **2** is possibly extending from the W centre towards the diazoalkane ligand as elucidated for the relating diazoalkane complexes [WCl$_2$(NN=CH$_2$)(PH$_3$)$_3$] and [WCl$_2$(C$_2$H$_4$)(NN=CH$_2$)(PH$_3$)$_2$],[1] the reduction of **2** is expected to produce the species with a reactive MNN=CRR′ moiety.

By treatment with an excess of Mg in thf at room temperature under CO, **2** afforded a ditungsten complex containing the bridging N=NCMe$_2$CMe$_2$N=N ligand [WCl(CO)$_2$(PMe$_2$Ph)$_2$(N=NCMe$_2$CMe$_2$N=N)WCl(CO)$_2$(PMe$_2$Ph)$_2$] **4**, which was isolated in 28% yield as brown crystals [eqn. (2)].‡ The PMe$_2$Ph ligand *trans* to the CO ligand in the starting diazoalkane complex **2** was replaced by CO during the coupling reaction. In contrast, complexes **1** and **3** were not reduced under the same reaction conditions, which is consistent with the electrochemical results described above. The structure of **4** was unambiguously determined by the X-ray analysis.§ As shown in Fig. 1, **4** has two W centres linked by a N=NCMe$_2$CMe$_2$N=N bridge resulting from the intermolecular coupling of the two diazoalkane ligands in **2** and the molecule has a C_2 symmetry around the axis bisecting the centre of the C(1)–C(1)* bond.

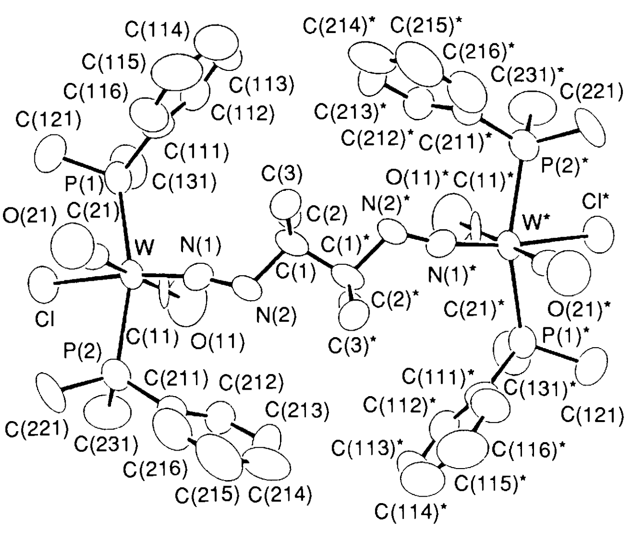


Fig. 1 Perspective view of **4**, viewed down the C_2 symmetry axis. Selected bond distances (Å) and angles (°) are as follows: W–N(1) 1.78(1), N(1)–N(2) 1.27(1), N(2)–C(1) 1.54(2), C(1)–C(1)* 1.56(3); W–N(1)–N(2) 168(1), N(1)–N(2)–C(1) 120(1), N(2)–C(1)–C(1)* 104(1).

The structural parameters in the W–N(1)–N(2)–C(1) moiety including the W–N(1)–N(2) angle of 168(1)°, the N(1)–N(2)–C(1) angle of 120(1)°, the N(1)–N(2) bond distance of 1.27(1) Å and the N(2)–C(1) distance of 1.54(2) Å are consistent with those of the organodiazenido ligand in [MoI(NNC$_6$H$_{11}$)(dppe)$_2$].[8] The W atom has an octahedral configuration, in which the Cl ligand coordinates *trans* to this diazenido ligand.

Previously, Pickett *et al.* reported briefly that the similar intermolecular coupling of the diazoalkane complex [WF(NN=CH$_2$)(dppe)$_2$]BF$_4$ takes place under electroreductive conditions to give [WF(dppe)$_2$(N=NCH$_2$CH$_2$N=N)WF(dppe)$_2$],[9] but the details of the structure of this diazenido complex were not available. Now the formation of the dinuclear diazenido complex **4** from the diazoalkane complex **2** under reductive conditions has been unambiguously demonstrated. Complex **4** is the first diazenido complex derived from the monophosphine dinitrogen complexes *cis*-[M(N$_2$)$_2$(PMe$_2$Ph)$_4$],¶ although a series of alkyl- or acyl-diazenido complexes of the type [MX(NNR)(dppe)$_2$][11,12] and

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‡ *Spectroscopic data* for **2**: ^{1}H NMR (CDCl$_3$) δ 1.91, 1.77 [t, 6H each, *J*(PH) 4.0 Hz, P*Me*$_2$Ph], 1.55 [d, 6H, *J*(PH) 8.5 Hz, P*Me*$_2$Ph], 1.80, 1.63 (s, 3H each, NNC*Me*$_2$); ^{31}P{^{1}H} NMR (CDCl$_3$, relative to H$_3$PO$_4$) δ −20.44 [d, *J*(WP) 266, *J*(PP′) 20 Hz], −23.60 [t, *J*(WP) 251 Hz]; IR (ν/cm^{-1}) ν(CO) 1990, ν(C=N) 1582. For **4**: ^{1}H NMR (C$_6$D$_6$) δ 1.88 [t, 24H, *J*(PH) 4.0 Hz, P*Me*$_2$Ph], 0.68 (s, 12H, NNC*Me*$_2$); IR (ν/cm^{-1}) ν(CO) 1990w, 1870vs, ν(N=N) 1590.

§ *Crystal data* for **4**: C$_{42}$H$_{56}$N$_4$O$_4$P$_4$Cl$_2$W$_2$, *M* = 1243.44, monoclinic, *C*2/*c*; *a* = 27.599(14), *b* = 12.904(8), *c* = 14.403(5) Å, β = 100.51(3)°, *V* = 5043 Å^3, *Z* = 4. D_c = 1.638 g cm^{-3}, μ(Mo-Kα) = 49.28 cm^{-1}, *F*(000) = 2440. *R* = 0.053 and R_w = 0.034 for 2102 reflections [$I > 2.5\sigma(I)$]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

¶ A BPh$_3$ adduct [WHClBr{=N=N(→BPh$_3$)H}(PMe$_2$Ph)$_3$] was isolated and characterized previously.[10]

$[MX(NNCOR)(dppe)_2]$[11,13] have been already prepared from the corresponding diphosphine dinitrogen complexes *trans*-$[M(N_2)_2(dppe)_2]$.

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