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Note

Synthesis and structures of tungsten ferrocenyldiazoalkane complexes derived from a dinitrogen complex. Part 58. Preparation and properties of molybdenum and tungsten dinitrogen complexes¹

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Abstract

Reaction of the hydrazido(2-) complex *cis*, *mer*-[WCl₂(NNH₂)(PMe₂Ph)₃], derived from a dinitrogen complex *cis*-[W(N₂)₂(PMe₂Ph)₄], with formylferrocene or acetylferrocene gave ferrocenyldiazoalkane complexes *cis*, *mer*-[WCl₂(NN=CRFc)(PMe₂Ph)₃] (**2**: R = H, Me; Fc = (η^5 -C₅H₄)Fe(η^5 -C₅H₅)). Treatment of **2** with π -acceptor ligands L such as CO, CH₂=CH₂, *p*-MeC₆H₄CHO, *p*-MeC₆H₄C≡CH and Bu^tNC afforded a series of ferrocenyldiazoalkane complexes *cis*, *trans*-[WCl₂(NN=CRFc)(L)(PMe₂Ph)₂] (**4**), while upon treatment with CH₂Cl₂ **2** gave the W(V) complexes *mer*, *trans*-[WCl₃(NN=CRFc)(PMe₂Ph)₂] (**5**). The X-ray analyses have been undertaken to determine the detailed structures for **2a** (R = H) and **5b** (R = Me). © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Crystal structures; Tungsten complexes; Dinitrogen complexes; Diazoalkane complexes; Ferrocenyl complexes

1. Introduction

The C-N bond formation at coordinated dinitrogen is a crucial step to achieve synthesis of organo-nitrogen compounds from molecular nitrogen under mild conditions [2-4]. However, there is only a limited number of dinitrogen complexes where the N2 ligand is transformed into an organo-nitrogen ligand or released from the metal as an organo-nitrogen compound. It is noteworthy that the Mo and W dinitrogen complexes *trans*- $[M(N_2)_2(dppe)_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) and $cis-[M(N_2)_2(PMe_2Ph)_4]$ (M = Mo, W) exhibit exceptionally high reactivities of the coordinated dinitrogen which result in the C-N bond formation along with the protonation at the N₂ ligand. One of the most potential methods to convert the N2 ligand into organonitrogen ligands is demonstrated by the syntheses of diazoalkane complexes such as *trans*- $[MF(NN=CRR')(dppe)_2]^+$ [5,6] and cis, mer-[MX₂(NN=CRR')(PMe₂Ph)₃] (1; X =halogen) [7,8] via condensation of aldehydes or ketones with the hydrazido(2-) complexes *trans*- $[MF(NNH_2)- (dppe)_2]^+$

or *cis*, *mer*- $[MX_2(NNH_2)(PMe_2Ph)_3]$, readily accessible from the N₂ complexes. Much effort has been made in quest of the versatile methods to liberate the diazoalkane ligands as organo-nitrogen compounds.

In this article we wish to report the syntheses, structures, and properties of the ferrocenyldiazoalkane complexes *cis*, *mer*-[WCl₂(NN=CRFc)(PMe₂Ph)₃] (**2a**: R = H; **2b**: R = Me; Fc = (η^{5} -C₅H₄)Fe(η^{5} -C₅H₅)) and their derivatives, which demonstrate a new feature of the diazoalkane ligand arising from the presence of the easily oxidizable and sterically bulky ferrocenyl substituent.

2. Experimental

2.1. General methods

All manipulations were performed under an atmosphere of nitrogen using standard Schlenk techniques. Solvents were dried and distilled by common procedures and then degassed before use. The hydrazido(2-) complex *cis*, *mer*-[WCl₂(NNH₂)(PMe₂Ph)₃] (**3**) was prepared by literature methods [9]. Formylferrocene (FcCHO) and acetylferrocene

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(FcCOMe) were obtained from Aldrich Chemical, or Tokyo Chemical Industry. Spectroscopic measurements and the elemental analyses were done as described previously [1]. Electrochemical data were collected as reported elsewhere [10]. In the ¹H NMR data below, the signals due to the phenyl protons are omitted.

2.2. Preparation of cis, mer-[WCl₂(NN=CRFc) (PMe₂Ph)₃] (2a: R = H; 2b: R = Me)

To an orange suspension of **3** (100 mg, 0.143 mmol) in CH_2Cl_2 (5 cm³) 2 equiv. of FcCHO or FcCOMe were added, and the mixture was stirred at room temperature for 5 h in the presence of a catalytic amount of aqueous HCl. The resultant purple solution was evaporated to dryness in vacuo and the residue was washed with ether to remove the unreacted FcCHO or FcCOMe. The remaining solid was crystallized from CH_2Cl_2 -hexane to yield the purple crystals of **2**, which were filtered off, washed with hexane, and then dried in vacuo.

2a. Yield: 84%. *Anal.* Calc. for $C_{35}H_{43}N_2Cl_2P_3FeW$: C, 46.96; H, 4.84; N, 3.13. Found: C, 46.86; H, 4.89; N, 3.19%. IR (KBr): ν (C=N), 1551 cm⁻¹. ¹H NMR (C₆D₆): δ 4.40 and 4.13 (t, 2H each, J = 2.0 Hz, C_5H_4), 3.99 (s, 5H, Cp), 2.11 and 1.74 (t, 6H each, $J_{P-H} = 3.6$ Hz, PMe), 1.58 (d, 6H, $J_{P-H} = 8.6$ Hz, PMe). The methine resonance seems to be overlapping with the signals of the phenyl protons.

2b. Yield: 88%. *Anal.* Calc. for $C_{36}H_{45}N_2P_3Cl_2FeW$. 0.5CH₂Cl₂: C, 46.06; H, 4.87; N, 2.94. Found: C, 46.68; H, 5.07; N, 3.02%. IR (KBr): ν (C=N), 1530 cm⁻¹. ¹H NMR (C₆D₆): δ 4.53 and 4.14 (m, 2H each, C₅H₄), 3.97 (s, 5H, Cp), 2.02 (s, 3H, NN=CMe), 1.97 and 1.81 (t, 6H each, $J_{P-H} = 3.6$ Hz, PMe), 1.60 (d, 6H, $J_{P-H} = 8.6$ Hz, PMe).

2.3. Preparation of cis, trans-[WCl₂(NN=CRFc)(L) (PMe₂Ph)₂](4)

On treatment with CO (1 atm), $CH_2=CH_2$ (1 atm), p-MeC₆H₄CHO (4 equiv.), p-MeC₆H₄C=CH (1 equiv.) or Bu^tNC (1 equiv.) in THF at 55°C for 16–24 h, the purple solution of **2** turned dark purple. The resulting solution was dried up in vacuo and the residue was crystallized from CH₂Cl₂-hexane to give purple crystals of **4**, which were filtered off, washed with hexane, and then dried in vacuo.

4a (R = H, L = CO). Yield: 92%. *Anal.* Calc. for $C_{28}H_{32}N_2OCl_2P_2FeW$: C, 42.84; H, 4.11; N, 3.57. Found: C, 42.96; H, 4.05; N, 3.88%. IR (KBr): ν (CO), 1934; ν (C=N), 1541 cm⁻¹. ¹H NMR (C₆D₆): δ 4.11 and 3.99 (m, 2H each, C₅H₄), 3.73 (s, 5H, Cp), 1.87 and 1.85 (t, 6H each, $J_{P-H} = 4.0$ Hz, PMe).

4b (R = H, L = η²-CH₂=CH₂). Yield: 88%. *Anal.* Calc. for C₂₉H₃₆N₂OP₂Cl₂FeW: C, 44.36; H, 4.62; N, 3.57. Found: C, 43.83; H, 4.76; N, 3.51%. IR (KBr): ν (C=N), 1551 cm⁻¹. ¹H NMR (C₆D₆): δ 4.26 and 4.11 (t, 2H each, J = 2.0 Hz, C₅H₄), 3.90 (s, 5H, Cp), 2.18–1.94 (m, 4H, C₂H₄), 2.11 and 1.90 (t, 6H each, $J_{P-H} = 4.3$ Hz, PMe). **4c** (R = H, L = η^2 -*p*-MeC₆H₄CHO). Yield: 78%. Anal. Calc. for C₃₅H₄₀N₂OCl₂P₂FeW: C, 47.92; H, 4.60; N, 3.19. Found: C, 47.97; H, 5.02; N, 2.95%. IR (KBr): ν (C=N), 1543 cm⁻¹. ¹H NMR (C₆D₆): δ 5.18 (d, 1H, *J* = 9.9 Hz, MeC₆H₄CHO), 4.26 and 4.13 (m, 1H each, C₅H₄), 4.10 (m, 2H, C₅H₄), 4.02 (s, 5H, Cp), 2.26 (s, 3H, *Me*C₆H₄CHO), 2.09 (d, 3H, *J*_{P-H} = 9.9 Hz, PMe), 2.02 (d, 6H, *J*_{P-H} = 10.2 Hz, PMe), 1.87 (d, 3H, *J*_{P-H} = 9.2 Hz, PMe).

4d (R = H, L = η^2 -*p*-MeC₆H₄C=CH). Yield: 63%. Anal. Calc. for C₃₆H₄₀N₂Cl₂P₂FeW: C, 49.51; H, 4.62; N, 3.21. Found: C, 50.12; H, 5.06; N, 3.04%. IR (KBr): ν (C=C), 1728; ν (C=N) 1541 cm⁻¹. ¹H NMR (C₆D₆): δ 9.77 (dd, 1H, J = 16.5 and 5.6 Hz, MeC₆H₄C=CH), 4.37 and 4.23 (m, 1H each, C₅H₄), 4.08 (m, 2H, C₅H₄), 3.97 (s, 5H, Cp), 2.17, 2.14, 2.05 and 1.67 (d, 3H each, J_{P-H} = 9.9 Hz, PMe), 2.11 (s, 3H, MeC_6H_4C =CH).

4e (R = H, L = Bu^tNC). Yield: 94%. *Anal.* Calc. for $C_{32}H_{44}N_3Cl_2P_2FeW$: C, 45.74; H, 4.92; N, 5.00. Found: C, 45.12; H, 5.15; N, 4.86%. IR (KBr): ν (C=N), 2127 and 1910 (br); ν (C=N), 1545 cm⁻¹. ¹H NMR (C_6D_6): δ 4.31 and 4.09 (t, 2H each, J = 2.0 Hz, C_5H_4), 3.93 (s, 5H, Cp), 2.09 and 2.07 (t, 6H each, $J_{P-H} = 4.2$ Hz, PMe), 1.06 (s, 9H, Bu^tNC).

4f (R =Me, L = CO). Yield: 77%. *Anal.* Calc. for $C_{28}H_{32}N_2OCl_2P_2FeW$: C, 43.59; H, 4.29; N, 3.51. Found: C, 43.80; H, 4.33; N, 3.58%. IR (KBr): ν (CO), 1920; ν (C=N), 1510 cm⁻¹. ¹H NMR (C₆D₆): δ 4.33 and 4.06 (m, 2H each, C₅H₄), 3.81 (s, 5H, Cp), 1.94 (t, 12H, $J_{P-H} = 4.0$ Hz, PMe), 1.48 (s, 3H, NN=CMe).

4g (R = Me, L = η^2 -CH₂=CH₂). Yield: 80%. *Anal.* Calc. for C₃₀H₃₈N₂P₂Cl₂FeW: C, 45.09; H, 4.79; N, 3.51. Found: C, 44.78; H, 4.78; N, 3.51%. IR (KBr): ν (C=N), 1518 cm⁻¹. ¹H NMR (C₆D₆): δ 4.40 and 4.10 (t, 2H each, *J* = 2.0 Hz, C₅H₄), 3.92 (s, 5H, Cp), 2.13–2.03 (m, 4H, C₂H₄), 2.03 and 1.92 (t, 6H each, *J*_{P-H} = 4.3 Hz, PMe), 1.59 (s, 3H, NN=CMe).

4h (R =Me, L = η^2 -*p*-MeC₆H₄C=CH). Yield: 63%. *Anal.* Calc. for C₃₆H₄₀N₂Cl₂P₂FeW·CH₂Cl₂: C, 46.95; H, 4.56; N, 2.88. Found: C, 47.55; H, 4.73; N, 2.67%. IR (KBr): ν (C=C), 1736; ν (C=N), 1510 cm⁻¹. ¹H NMR (C₆D₆): δ 9.63 (dd, 1H, *J* = 16.5 and 5.8 Hz, MeC₆H₄C=CH), 4.49 and 4.41 (m, 1H each, C₅H₄), 4.14 (m, 2H, C₅H₄), 3.97 (s, 5H, Cp), 2.21–1.82 (total 18H, *Me*C₆H₄C=CH, PMe, and NN=CMe).

4i (R = Me, L = Bu^tNC). Yield: 70%. *Anal.* Calc. for $C_{32}H_{44}N_3Cl_2P_2FeW$: C, 46.40; H, 5.07; N, 4.92. Found: C, 46.01; H, 5.21; N, 4.62%. IR (KBr): ν (C=N), 2091; ν (C=N) 1518 cm⁻¹. ¹H NMR (C₆D₆): δ 4.46 and 4.09 (m, 2H each, C₅H₄), 3.89 (s, 5H, Cp), 2.08 and 2.05 (t, 6H each, $J_{P-H} = 4.0$ Hz, PMe), 1.70 (s, 3H, NN=CMe), 1.05 (s, 9H, Bu^tNC).

2.4. Preparation of mer, trans-[WCl₃(NN=CRFc) (PMe₂Ph)₂](5)

A purple solution of **2** in THF (5 cm³)-CH₂Cl₂ (3 cm³) kept at 55°C gradually turned dark purple. After 16 h, the

Table	1					
X-ray	crystallographic	data	for	2a	and	5b

2a	5b
C35H43N2Cl2P3FeW	C ₂₈ H ₃₄ N ₂ P ₂ Cl ₃ FeW
895.26	806.59
red-purple	purple
$0.2 \times 0.3 \times 0.6$	0.5 imes 0.7 imes 0.7
monoclinic	monoclinic
C2/c (no. 15)	$P2_1/n$ (no. 14)
25.893(3)	13.318(2)
9.959(5)	12.467(2)
28.825(3)	19.068(2)
91.015(8)	103.589(7)
7431(3)	3077.4(6)
8	4
1.60	1.741
37.86	45.95
3568	1588
Mo Kα (0.7107 Å)	Mo Kα (0.7107 Å)
graphite	graphite
room temperature	room temperature
$\omega/2\theta$	$\omega/2\theta$
16	16
55	55
9008	7395
1.003-1.075	0.4138-1.000
nements	
5718 $(I > 5\sigma(I))$	5423 $(I > 3\sigma(I))$
397	335
0.033, 0.022	0.032, 0.023
	2a $C_{35}H_{43}N_2Cl_2P_3FeW$ 895.26 red-purple 0.2 × 0.3 × 0.6 monoclinic C2/c (no. 15) 25.893(3) 9.959(5) 28.825(3) 91.015(8) 7431(3) 8 1.60 37.86 3568 Mo Kα (0.7107 Å) graphite room temperature $\omega/2\theta$ 16 55 9008 1.003–1.075 mements 5718 (I > 5 $\sigma(I)$) 397 0.033, 0.022

resultant solution was evaporated to dryness and the residue was crystallized from CH_2Cl_2 -hexane to give purple crystals of **5**, which were filtered off, washed with hexane, and then dried in vacuo.

5a (R = H). Yield: 54%. Anal. Calc. for $C_{27}H_{32}N_2Cl_3$ -P₂FeW: C, 40.92; H, 4.07; N, 3.53. Found: C, 40.40; H, 4.23; N, 3.56%. IR (KBr): ν (C=N) 1541 cm⁻¹.

5b (R = Me). Yield: 69%. Anal. Calc. for $C_{28}H_{34}N_2Cl_3$ -P₂FeW: C, 41.69; H, 4.25; N, 3.47. Found: C, 41.64; H, 4.30; N, 3.41%. IR (KBr): ν (C=N) 1510 cm⁻¹.

2.5. X-ray crystallographic studies of 2a and 5b

The X-ray diffraction studies were undertaken as described in the previous paper [1]. The crystallographic data for 2a and 5b are summarized in Table 1.

3. Results and discussion

3.1. Preparation of ferrocenyldiazoalkane complexes 2

Reaction of the hydrazido(2-)complex 3, readily derived from $cis-[W(N_2)_2(PMe_2Ph)_4]$, with 2 equiv. of FcCHO or FcCOMe in CH₂Cl₂ proceeded smoothly at room temperature in the presence of a catalytic amount of aqueous HCl to give the purple ferrocenyldiazoalkane complexes 2a and 2b in 84 and 88% yields, respectively (Scheme 1). This procedure is essentially similar to that for preparing 1 (X = CI)by condensation between 3 and common aldehydes or ketones [7,8]. In the IR spectra, the intense bands assignable to ν (C=N) appeared at 1551 and 1530 cm⁻¹ for **2a** and **2b**, respectively, which are comparable to the values observed for 1 (R = Ph, R' = H or Me), e.g. *cis*, *mer*-[WCl₂(NN= CHPh)(PMe₂Ph)₃]: 1535 cm⁻¹ [10] and *cis*, *mer*-[WBr₂- $(NN=CMePh)(PMe_2Ph)_3$]: 1537 cm⁻¹ [7]. The ¹H NMR spectra of 2 show the resonances due to the ferrocenyl group in addition to the signals ascribable to the three PMe₂Ph ligands. Appearance of the methyl protons in these PMe₂Ph ligands as two triplets and one doublet indicates the meridional configuration of the three PMe₂Ph ligands. These spectroscopic data suggest that complexes 2 have the structure shown in Scheme 1, which has been further confirmed by the X-ray analysis of 2a (vide infra).



Scheme 1.

3.2. Reactions of ferrocenyldiazoalkane complexes 2

In the course of our study to clarify the reactivities of **1**, we have previously found that new diazoalkane complexes such as cis, trans- $[MX_2(NN=CRR')(L)(PMe_2Ph)_2]$ [10,11] and mer, trans-[WX₃(NN=CRR')(PMe₂Ph)₂] [12] are further available from 1, although the diazoalkane ligands are left intact in these complexes in spite of either the coordination of various π -acceptor ligands L in the *cis* position for the former or the oxidation of the W center for the latter. It has been shown that 2 reacts analogously with various π -acceptor ligands L (L = CO, C₂H₄, p- MeC_6H_4CHO , p-MeC₆H₄C=CH, or Bu^tNC) to give a series of diazoalkane complexes cis, trans-[WCl2(NN=CRFc)- $(L)(PMe_2Ph)_2$] (4) in moderate to high yields, where the PMe₂Ph ligand being cis to the diazoalkane ligand and trans to one Cl in 2 is selectively replaced by L (Scheme 1). The spectroscopic data observed for 4 are comparable to those of similar compounds cis, trans-[WCl2(NN=CRMe)(L)- $(PMe_2Ph)_2$ (R = Me, Ph) reported previously [10].

Treatment of **2** with excess CH₂Cl₂ in THF at 55°C yielded the paramagnetic **5a** and **5b** in 54 and 69% yields, respectively (Scheme 1). The presence of the diazoalkane ligands is implicated by the ν (C=N) bands at 1541 and 1510 cm⁻¹ in the IR spectra. The X-ray diffraction study of **5b** has been carried out to confirm the structure as described below.

3.3. Structures of 2a and 5b

The detailed structures of 2a and 5b have been determined by X-ray crystallography. The ORTEP drawings are depicted in Figs. 1 and 2, while the selected bond distances and angles are listed in Table 2. Both complexes have a slightly distorted octahedral structure, in which the diazoalkane ligand occupies the position trans to one of the Cl ligands. In 2a three PMe₂Ph ligands are mutually meridional, whereas **5b** has a structure resulting from the replacement of the unique PMe₂Ph ligand in 2a by the Cl ligand. The W–Cl bond lengths in the W(V) complex 5b (2.400(1), 2.465(1), and 2.408 Å) are slightly shorter than those in the W(IV) complex 2a (2.466(1) and 2.533 Å), while the W-P distances in the former (2.549(1) and 2.565(1) Å) are somewhat elongated from those in the latter (2.492(2), 2.454(1),and 2.527(1) Å). Pertinent bonding parameters in the ferrocenyldiazoalkane ligand are similar to each other for 2a and 5b; the W-N-N linkage is essentially linear (2a: $173.3(1)^{\circ}$, **5b**: $169.3(3)^{\circ}$), while the N–N–C moiety is bent with the angles of $115.4(4)^{\circ}$ for **2a** and $119.2(4)^{\circ}$ for **5b**. In both complexes, the ferrocenyl group is bound to the C=N bond so as to be oriented to the exo direction presumably because of the steric bulkyness. The W, N(1), N(2), and C(25) (in 2a) or C(2) (in 5b) atoms, together with the Cp ring attached to this C atom are essentially coplanar. The observed N-N and N-C bond lengths, viz. d (N-N): 2a, 1.360(5) Å; **5b**, 1.313(5) Å and d (N–C): **2a**, 1.284(5) Å; **5b**,



Fig. 1. Molecular structure of 2a. Carbon atoms in the PMe₂Ph ligands and all hydrogen atoms are omitted for clarity.



Fig. 2. Molecular structure of 5b. Carbon atoms in the PMe₂Ph ligands and all hydrogen atoms are omitted for clarity.

1.298(5) Å, are almost comparable to those of the related diazoalkane ligands reported previously; e.g. d (N–N): 1.29(2) and d (N–C): 1.27(2) Å in *cis*, *trans*-[WCl₂(NN=CMPh)(η^2 -p-MeC₆H₄CHO)(PMe₂Ph)₂] [10] and d (N–N): 1.27(1) and d (N–C): 1.30(2) Å in *mer*, *trans*-[WBr₃(NN=CMPh)(PMe₂Ph)₂] [12], although the N–N distance in **2a** is somewhat longer. By comparison, the values observed in the hydrazones of FcCHO relevant to **2a** and **5b** are, e.g., FcCH=NNH(C₅H₄N-2): d (N–N), 1.368(5); d (N–C),

Selected bond lengths (A) and angles () in 2a and 50						
2.466(1)	W-Cl(2)	2.533(1)				
2.492(2)	W-P(2)	2.454(1)				
2.527(1)	W-N(1)	1.736(4)				
1.360(5)	N(2)-C(25)	1.284(5)				
88.04(5)	Cl(1)-W-P(1)	87.03(5)				
86.83(5)	Cl(1)-W-P(3)	84.61(5)				
174.3(1)	Cl(2)-W-P(1)	80.82(5)				
174.48(5)	Cl(2)-W-P(3)	84.69(5)				
97.6(1)	P(1)-W-P(2)	96.91(5)				
163.64(5)	P(1)-W-N(1)	92.9(1)				
96.85(5)	P(2)-W-N(1)	87.5(1)				
96.5(1)	W-N(1)-N(2)	173.3(1)				
115.5(4)	N(2)-C(25)-C(26)	121.8(4)				
2.400(1)	W-Cl(2)	2.465(1)				
2.408(1)	W-P(1)	2.549(1)				
2.565(1)	W-N(1)	1.763(4)				
1.313(5)	N(2)–C(2)	1.298(5)				
86.60(5)	Cl(1)-W-Cl(3)	170.82(5)				
88.24(4)	Cl(1)-W-P(2)	81.75(4)				
98.2(1)	Cl(2)-W-Cl(3)	85.04(5)				
84.39(4)	Cl(2)-W-P(2)	87.52(4)				
175.1(1)	Cl(3)-W-P(1)	87.17(5)				
101.66(5)	Cl(3)-W-N(1)	90.1(1)				
167.48(5)	P(1)-W-N(1)	94.6(1)				
93.4(1)	W-N(1)-N(2)	169.3(3)				
119.2(4)	N(2)-C(2)-C(1)	123.8(5)				
116.5(4)	C(1)-C(2)-C(3)	119.7(4)				
	$\begin{array}{c} 2.466(1)\\ 2.492(2)\\ 2.527(1)\\ 1.360(5)\\ \\ 88.04(5)\\ 86.83(5)\\ 174.3(1)\\ 174.48(5)\\ 97.6(1)\\ 163.64(5)\\ 96.85(5)\\ 96.5(1)\\ 115.5(4)\\ \\ \hline \\ 2.400(1)\\ 2.565(1)\\ 1.313(5)\\ \\ 86.60(5)\\ 88.24(4)\\ 98.2(1)\\ 84.39(4)\\ 175.1(1)\\ 101.66(5)\\ 167.48(5)\\ 93.4(1)\\ 119.2(4)\\ 116.5(4)\\ \end{array}$	and angles () in 24 and 30 2.466(1) W-Cl(2) 2.492(2) W-P(2) 2.527(1) W-N(1) 1.360(5) N(2)-C(25) 88.04(5) Cl(1)-W-P(1) 86.83(5) Cl(1)-W-P(3) 174.3(1) Cl(2)-W-P(1) 174.48(5) Cl(2)-W-P(3) 97.6(1) P(1)-W-P(2) 163.64(5) P(1)-W-N(1) 96.5(1) W-N(1)-N(2) 115.5(4) N(2)-C(25)-C(26) 2.400(1) W-Cl(2) 2.408(1) W-P(1) 2.565(1) W-N(1) 1.313(5) N(2)-C(2) 86.60(5) Cl(1)-W-Cl(3) 88.24(4) Cl(1)-W-P(2) 98.2(1) Cl(2)-W-P(2) 175.1(1) Cl(3)-W-P(1) 101.66(5) Cl(3)-W-N(1) 167.48(5) P(1)-W-N(1) 93.4(1) W-N(1)-N(2) 119.2(4) N(2)-C(2)-C(1) 116.5(4) C(1)-C(2)-C(3)				

Table 2 Selected bond lengths (Å) and angles (°) in **2a** and **5b**

1.274(5) Å [13] and FcCH=NN=CHC₆H₄NO₂-*p*: *d* (N–N), 1.410(6); *d* (N–C), 1.272(7) Å [14].

3.4. Electrochemical properties of 2 and 4

The cyclic voltammogram of 2a exhibits a reversible oxidation wave due to the W(IV)/W(V) couple at the anodic peak potential E_p^{ox} at 0.15 V versus SCE together with an irreversible oxidation wave attributable to the Fe(II)/Fe(III) couple at $E_p^{ox} = 1.13$ V. The former value is in good agreement with the E_p^{ox} value assigned to the W(IV)/W(V) process of 0.13 V observed for **1a** (X = Cl, R = R' = Me) [10]. In the previous paper, we have reported that the HOMO (d_{xy} orbital of the W atom) in **1a** is significantly stabilized by the replacement of the unique PMe₂Ph ligand in the *x*-*y* plane with π -acceptor ligands L such as CO and CH₂=CH₂, resulting in the shift of the $E_{1/2}^{ox}$ values to the positive direction in these derivatives cis, trans-[WCl₂(NN=CMe₂)(L)(PMe₂Ph)₂] [10]. Analogous trend was also observed for the potential due to the W(IV)/ W(V) couple in 4, as summarized in Table 3. On the other hand, the oxidation wave arising from the process $Fe(II) \rightarrow Fe(III)$ in 4 appeared at the same potential as in 2.

Table 3
Oxidation potentials of diazoalkane complexes ^a

L	WCl ₂ (NN=CHFc)- (L)(PMe ₂ Ph) ₂	WCl ₂ (NN=CMe ₂)- (L)(PMe ₂ Ph) ₂ ^{c}		
PMe ₂ Ph	0.15 (r), 1.13 (ir)	0.13 (r)		
CO	0.68, 1.05 (ir)	0.98 (ir)		
C_2H_4	1.15 (ir) ^b	1.20 (ir)		

^a In CH₂Cl₂–0.1 M [^{*n*}Bu₄N][BF₄]. Peak oxidation potential vs. SCE at a scan rate 200 mV s⁻¹. (r)=reversible and (ir)=irreversible process. ^b The peaks due to W(IV)/W(V) and Fe(II)/Fe(III) couples are overlapping.

^c Ref. [10].

4. Supplementary material

Detailed data of the X-ray crystallographic studies for **2a** and **5b**, which include Tables of atomic coordinates, anisotropic temperature factors of non-hydrogen atoms, and extensive bond distances and angles, together with Figures showing their full view, are available from the authors (Y.M. or M.H.) upon request.

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