On the structure, carbonyl-stretching frequencies and relative stability of *trans*- and *cis*-[W(CO)$_4$(η^2-alkene)$_2$]$^{0/+}$: a theoretical and IR spectroelectrochemical study†

Jarosław Handzlik,^{a} Frantisek Hartl*^{b} and Teresa Szymańska-Buzar*^{c}

^{a} *Institute of Organic Chemistry and Technology, Cracow University of Technology, 31-155 Kraków, Poland*

^{b} *Institute of Molecular Chemistry, Universiteit van Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands. E-mail: hartl@science.uva.nl; Fax: +31 20 525 6456; Tel: +31 20 525 6450*

^{c} *Faculty of Chemistry, University of Wrocław, 14 F. Joliot-Curie, 50-383 Wrocław, Poland. E-mail: tsz@wchuwr.chem.uni.wroc.pl; Fax: +48 71 3282348; Tel: +48 71 3204221*

The geometries, v(CO) frequencies, relative enthalpies and Gibbs energies of the alkene carbonyl complexes [W(CO)$_4$(η^2-C$_2$H$_4$)$_2$]$^{0/+}$ and [W(CO)$_5$(η^2-C$_2$H$_4$)] were calculated by means of the GAUSSIAN 98 program using the hybrid B3-LYP density functional. The predicted geometries and v(CO) vibrational frequencies agree with the experimental data. The calculated relative energies (ΔG_{298}) show that *trans*-[W(CO)$_4$(η^2-C$_2$H$_4$)$_2$] is more stable by 10 or 12 kJ mol^{-1} (depending on the basis set applied) than *cis*-[W(CO)$_4$(η^2-C$_2$H$_4$)$_2$]. In contrast to this, the stability of their one-electron oxidation products, the corresponding 17-electron cationic complexes, is reversed, the cationic form of the *cis* isomer being preferred by 14 or 10 kJ mol^{-1}. Comparison of the calculated and experimental vibrational spectra has elucidated the electrochemical oxidation path of *trans*-[W(CO)$_4$(η^2-alkene)$_2$] compounds. The electrochemical oxidation of *trans*-[W(CO)$_4$(η^2-1-butene)$_2$] produces the corresponding 17-electron cation, which undergoes spontaneous isomerisation to *cis*-[W(CO)$_4$(η^2-1-butene)$_2$]$^+$. The identity of the latter species has been established by cyclic voltammetric and IR spectroelectrochemical experiments at low temperature.

Introduction

Zero-valent tungsten bis(alkene) complexes of the type *trans*-[W(CO)$_4$(η^2-alkene)$_2$], first characterised by IR spectroscopy by Stolz *et al.* in 1963,[1] remain the focus of much attention.[1–20] The structure of several *trans*-bis(alkene) complexes has been elucidated by X-ray crystallographic studies.[2,11,18,20] The two alkene ligands are mutually orthogonal and eclipsed with respect to the OC–W–CO axes of the square-planar W(CO)$_4$ unit. The neutral *cis*-bis(alkene) complexes were identified as transients at low temperatures[3,4,6,16–19] or in the gas phase.[13]

Studies of this class of complexes have focused on their participation as important intermediates in reactions of alkenes catalysed by transition metal carbonyls.[3,9,10,12,14–19] Of particular interest have been the catalytic cycles of [W(CO)$_6$] regarding isomerisation and metathesis reactions of alkenes.

The widely studied photochemical isomerisation of *trans*-[W(CO)$_4$(η^2-alkene)$_2$] complexes to their thermally unstable *cis* isomers can be monitored conveniently at low temperatures with IR and NMR spectroscopies.[16–19] Preliminary studies have revealed that the *trans–cis* isomerisation of *trans*-[W(CO)$_4$(η^2-alkene)$_2$] is also induced by one-electron electro-

chemical oxidation.[12] However, the cationic d^5 tungsten(I) product has only been identified in frozen electrolysed solution by EPR spectroscopy. In addition, the published voltammetric data have been ambiguous with regard to the more positively lying W^0/W^I redox couple for the *cis* isomers, hence pointing to the electrocatalytic nature of the *trans–cis* isomerisation. In this paper we rectify the assignment of the cyclic voltammetric response with support from an IR spectroelectrochemical study of the oxidation at variable temperatures and from theoretical calculations of structural parameters and IR v(CO) frequencies. In the case of transition metal carbonyls IR spectroscopy is often used to identify reactive intermediates. Comparison of calculated and experimental vibrational spectra has become one of the principal means of identifying unusual molecules. The low-spin d^5 chromium(I) cationic complex [Cr(CO)$_4$(3,4,7,8-tetramethyl-1,10-phenanthroline)]$^+$, thoroughly studied by combined low-temperature IR, UV-VIS and EPR spectroelectrochemical and DFT computational methods,[21] provides a suitable example.

Several previous theoretical studies dealt with *trans*-[Mo(CO)$_4$(η^2-C$_2$H$_4$)$_2$][22–24] and [W(CO)$_5$(η^2-C$_2$H$_4$)],[25,26] however, little is known about the structure of *cis*-[W(CO)$_4$(η^2-C$_2$H$_4$)$_2$] and of the corresponding cation. Understanding the factors controlling their conformational preferences is important, as various catalytic cycles for the transformation of olefins involve the W(CO)$_4$ unit with two organic ligands in mutually *cis* positions. In metathesis reactions of olefins, the formation of such catalytically active intermediates is expected, being induced by the oxidation of zero-valent tungsten compounds

---

† Electronic supplementary information (ESI) available: **Tables S1–S18** Cartesian coordinates for fully optimised geometries of *trans*-[W(CO)$_4$(η^2-C$_2$H$_4$)$_2$], *trans*-[W(CO)$_4$(η^2-C$_2$H$_4$)$_2$]$^+$, *cis*-[W(CO)$_4$(η^2-C$_2$H$_4$)$_2$], *cis*-[W(CO)$_4$(η^2-C$_2$H$_4$)$_2$]$^+$, [W(CO)$_5$(η^2-C$_2$H$_4$)], and [W(CO)$_6$], and their corresponding energies (E_0, H and G). See http://www.rsc.org/suppdata/nj/b1/b104786h/

by Lewis acids such as $SiCl_4$, $GeCl_4$ or $SnCl_4$.[27,28] Therefore, it has been our aim to explain and predict the geometry and relative stability of *trans*- and, in particular, *cis*-[W(CO)$_4$(η^2-alkene)$_2$] complexes and their 17-electron cationic forms. In the present paper, the theoretical part precedes the spectroelectrochemical study of the oxidation-induced *trans–cis* isomerisation.

Experimental

Materials

Dichloromethane (Acros; analytical quality) was dried over anhydrous $CaCl_2$ and freshly distilled under nitrogen. The supporting electrolyte Bu_4NPF_6 (Aldrich) was recrystallised twice from absolute ethanol and dried *in vacuo* at 80 °C for 10 h. The complexes *trans*-[W(CO)$_4$(η^2-alkene)$_2$], alkene = ethene (**1**) and 1-butene (**1A**), were synthesized by photochemical reaction of [W(CO)$_6$] with the alkene in *n*-hexane, according to published procedures.[17–19]

Computational details

Geometries. The geometries and v(CO) frequencies of the alkene carbonyl complexes *trans*-[W(CO)$_4$(η^2-C$_2$H$_4$)$_2$]$^{0/4}$ (**1**/**1$^+$**), *cis*-[W(CO)$_4$(η^2-C$_2$H$_4$)$_2$]$^{0/+}$ (**2**/**2$^+$**), and [W(CO)$_5$(η^2-C$_2$H$_4$)] (**3**), were calculated with the GAUSSIAN 98 program[29] by means of density functional theory (DFT). The hybrid B3-LYP density functional was applied in all calculations.[30] Two basis sets were employed in parallel. The first one, denoted A hereafter, includes a pseudopotential LANL2DZ basis set[31] for the W atom and a Dunning–Huzinaga valence double-ζ basis with a set of d-polarization functions D95V(d)[32] for the C, O and H atoms. In the second basis set denoted B, the W atom is also described by a LANL2DZ basis set, while other atoms are described by a 6-31G(d) basis. The calculations of the neutral complexes were carried out at the restricted B3-LYP level. The unrestricted B3-LYP approach was used in the case of the cationic forms. In all the cases, the stability of the wavefunction was tested.[33]

All the structures were fully optimised with the Berny algorithm using redundant internal coordinates.[34,35] The calculations were initially performed without any symmetry constraints. Then, the structures were optimised with the molecular symmetries obtained during the earlier calculations. In general, the B basis set yields slightly longer W–C bonds and shorter C=C, C–H and C≡O bonds than the A basis.

To estimate the accuracy of the theoretical method applied, the geometry calculations for the well-known structure of tungsten hexacarbonyl has been performed. The W–C bond lengths of 2.062 and 2.068 Å obtained, with the B3-LYP/A and B3-LYP/B methods, respectively, are consistent with the reported experimental value of 2.058 Å.[36] A similar accuracy for DFT calculations of the W–C bond lengths in [W(CO)$_6$] was obtained by Ziegler *et al.*[37,38]

Harmonic vibrational frequencies were calculated for each structure to confirm the potential energy minimum and to obtain v(CO) vibrational frequencies, enthalpies and Gibbs energies.

Vibrational spectra. The v(CO) frequencies were calculated employing the B3-LYP/B basis set. The scaling factor of 0.9614,[39] recommended for systems containing first and the second row elements at the B3-LYP/6-31G(d) level, was used after its re-examination to calculate v(CO) vibrations for [W(CO)$_6$] (2109 a$_{1g}$, 2019 e$_g$ and 1996 t$_{1a}$ cm^{-1}). Despite the fact that within the B basis the tungsten atom is not described by the 6-31G(d) basis set, the scaled values of the v(CO)

vibrational frequencies are in satisfactory agreement with the recorded experimental data.

Additionally, we obtained a new scaling factor of 0.9648 for the W–CO interactions by a least-squares fit of the calculated data to the experimental vibrational frequencies of [W(CO)$_6$].[40] Comparison of the values of the v(CO) vibration frequencies obtained using both scaling factors indicates that the scaling factor obtained by Scott and Radom[39] provides a better fit to experiment.

Electrochemistry

All (spectro)electrochemical experiments were conducted under an inert atmosphere of dry nitrogen or argon. Cyclic voltammetry was carried out with an EG&G PAR Model 283 potentiostat, using a gas-tight three single-compartment cell equipped with a carefully polished Pt disk (0.42 mm^2 apparent surface area) working, Pt gauze auxiliary and Ag wire pseudo-reference electrodes. The reported electrode potentials are given against the ferrocene/ferrocenium (Fc/Fc$^+$) redox couple used as an internal standard.

IR spectroelectrochemical experiments at variable temperature were performed with a previously described OTTLE cell on a Pt minigrid working electrode positioned between CaF$_2$ optical windows (*ca.* 0.1 mm optical path).[41] The course of the redox reactions was monitored with a Bio-Rad FTS 7 FT-IR instrument and thin-layer cyclic voltammetry. Potential control was achieved with a PA4 potentiostat (EKOM, Czech Republic). In a typical experiment the cell was loaded with a 10^{-3} M solution of the bis(alkene) complex **1A** in dichloromethane containing 0.3 M Bu_4NPF_6.

Results and discussion

Geometries and relative stability of the alkene carbonyl complexes of tungsten

***trans*-[W(CO)$_4$(η^2-alkene)$_2$] (1).** The coordination sphere of tungsten in *trans*-[W(CO)$_4$(η^2-alkene)$_2$] compounds represents a distorted octahedron with the two alkene molecules mutually *trans*, orthogonal and each C=C bond eclipsing one of the two OC–W–CO axes in the equatorial W(CO)$_4$ plane. This geometry has been documented by X-ray crystallographic studies for compounds containing ethene,[18] *cis*- and *trans*-cyclo-octene[11,20] and methyl acrylate[2] ligands. Selected optimised geometrical parameters are compared with experimental values in Table 1. The theoretically predicted structure has D_{2d} symmetry. The complete calculated geometry for **1** is given in the ESI. There is good agreement between the previous X-ray structure and the data calculated in this work (Fig. 1). Note that the theory has predicted strictly the same W–C(ethene) bond lengths for the two carbons atoms of the ethene ligand, even though the two experimental crystallographic values differ by 0.016 Å. The calculated W–C(ethene) bond lengths of 2.349 (A basis) and 2.362 Å (B basis) slightly exceed the experimental values reported for **1** [2.299(9) and 2.315(9) Å].[18] This difference is to be expected due to the presence of packing forces in the crystal lattice.

***cis*-[W(CO)$_4$(η^2-C$_2$H$_4$)$_2$] (2).** *cis*-Bis(alkene) complexes have been proposed as key intermediates in catalytic cycles for [W(CO)$_6$] catalysed reactions of alkenes. However, an exact structure for this kind of compound has not been determined by X-ray crystallographic studies up to now. In both condensed and gas phases, *cis*-[M(CO)$_4$(η^2-C$_2$H$_4$)$_2$] (M = Cr, Mo, W) is thought to have C_{2v} symmetry with the two parallel ethene ligands.[13,23] In contrast to this, no theoretical paper reporting the full geometry optimisation of a *cis*-bis(alkene)

Table 1 Selected experimental and calculated structural parameters for the *trans*-[W(CO)$_4$(η^2-alkene)$_2$]$^{0/+}$ complexes[a]

Alkene	Ref.	W–C(alkene)	W–CO	C=C	OC–W–CO	W–C–O
18-Electron complexes						
C$_2$H$_4$	B3-LYP/A[b]	2.349	2.050	1.418	174.24	179.54
	B3-LYP/B[b]	2.362	2.055	1.411	172.76	179.54
	X-Ray[18]	2.299(9), 2.315(9)	2.033(10), 2.045(9)	1.413(13)	171.8(7)	175.1(13), 176.2(14)
cis-C$_8$H$_{14}$	X-Ray[11]	2.36(1), 2.38(1)	2.01(1), 2.03(1)	1.39(1)	173.9(3), 174.8(3)	176(1), 177(1), 178(1)
trans-C$_8$H$_{14}$	X-Ray[20]	2.327(3), 2.328(3)	2.026(5), 2.049(4)	1.412(6), 1.424(5)	176.2(1), 176.6(1)	176.8(3), 177.9(3)
CH$_2$=CHCO$_2$CH$_3$	X-Ray[2]	2.292(8), 2.310(7)	2.062(9), 2.043(10)	1.416(11), 1.396(13)	172.5(3), 172.3(3)	177.8(8), 175.7(8)
		2.306(9), 2.292(9)	2.039(8), 2.034(8)			179.2(7), 173.9(8)
17-Electron complex						
C$_2$H$_4$	B3-LYP/A[b]	2.466	2.081	1.388	175.10	178.71
	B3-LYP/B[b]	2.483	2.086	1.381	176.85	178.77

[a] Bond lengths are given in angstroms, bond angles in degrees. [b] This work.
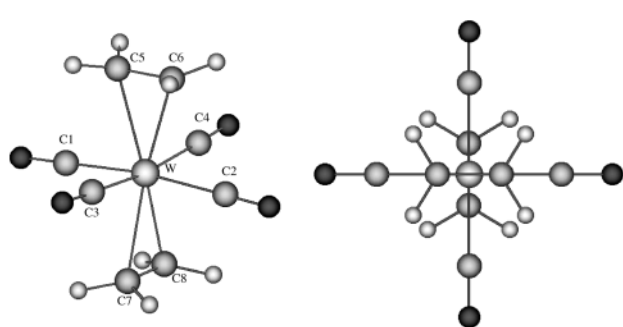
Fig. 1 Optimised geometry of *trans*-[W(CO)$_4$(η^2-C$_2$H$_4$)$_2$] (**1**).

metal carbonyl complex has appeared so far. In the present work, the calculations on the B3-LYP/A and B3-LYP/B level were carried out for several initial orientations of the two ethene ligands in **2**. We have localised four critical points on the potential energy surfaces.

Fig. 2 shows the four optimised structures of different symmetry: **2a** (*C*$_2$) **2a′** (*C*$_{2v}$) **2b** (*C*$_s$) with mutually perpendicular C=C bonds) and **2c** (*C*$_{2v}$, with both olefinic bonds in the equatorial plane). The **2a′** structure possesses the postulated *C*$_{2v}$ symmetry with two parallel ethene ligands. However, on the B3-LYP/B level, this structure is calculated to be a transition state with an imaginary frequency corresponding to the rotation of ethene ligands about the tungsten–ethene axes. This motion leads to the **2a** structure of *C*$_2$ symmetry. On the other hand, the **2a′** conformation is predicted to be a ground state at the B3-LYP/A level of calculations. The relative enthalpies and Gibbs energies of the four calculated conformers of **2** are given in Table 2. The results obtained for the **2a′** geometry on the B3-LYP/B level have been omitted. The conformation **2a** of *C*$_2$ symmetry with two slightly staggered C=C bonds has the lowest enthalpy, but the enthalpies predicted for the **2a′** and **2b** conformers is only about 1 kJ mol^{-1} higher. On the other hand, the predicted Gibbs energy difference between the four conformers indicates that **2a′** is thermodynamically favoured in comparison to **2b** and **2a**. However, the presented differences are very low (in the range of 1–3 kJ mol^{-1}) and their order could possibly reversed if different theoretical methods are applied. Therefore, on the basis of the current calculations, it seems that both **2a** (or **2a′**) and **2b** structures cannot be excluded as the most stable conformation. The third structure (**2c**) has clearly both higher enthalpy and Gibbs energy compared to the **2a**, **2a′** and **2b** conformers. Complete results of the thermochemical analysis of the calculated possible conformers of **2** are given in the ESI.
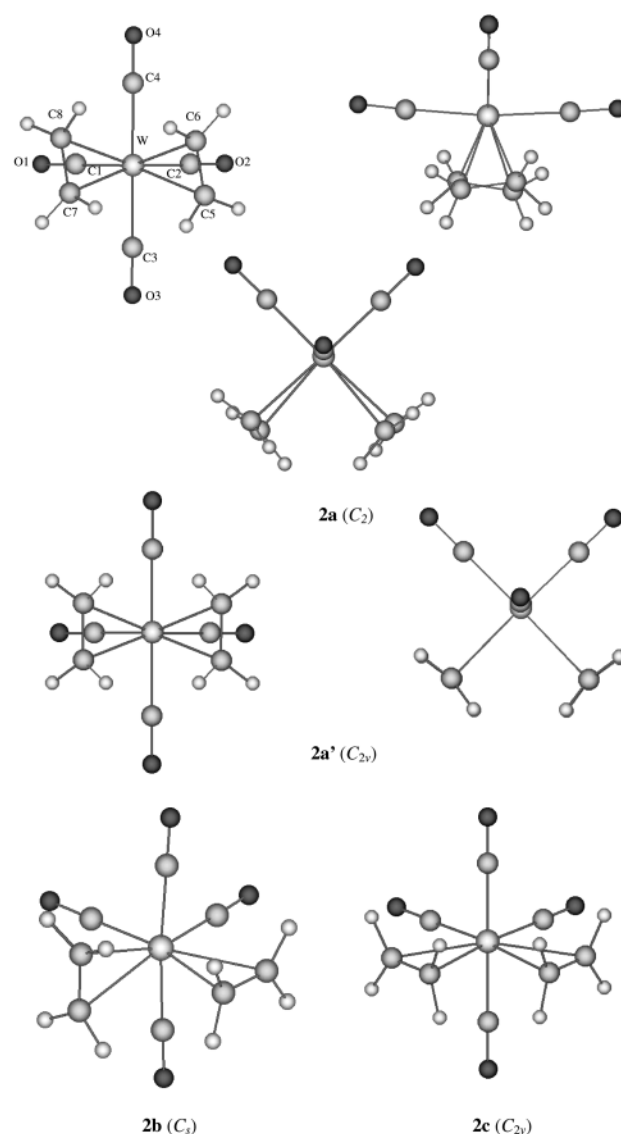
Fig. 2 Theoretically predicted geometries for *cis*-[W(CO)$_4$(η^2-C$_2$H$_4$)$_2$] (**2**).

Selected structural parameters for **2a** are presented in Table 3. The complete data for all four possible conformers of **2** are given in the ESI. The two carbons in each ethene ligand in **2a** are bound at slightly different distances to tungsten (2.479 and 2.466 Å for B3-LYP/A, and 2.490 and 2.474 Å for B3-LYP/B). The two mutually *trans* carbonyls bind at a longer

Table 2 Enthalpies and Gibbs energies (kJ mol^{-1}) calculated for the four idealised conformations of cis-[W(CO)$_4$(η^2-C$_2$H$_4$)$_2$] **2** relative to **2a**

	Method	**2a** (C_2)	**2a′** (C_{2v})	**2b** (C_s)	**2c** (C_{2v})
ΔH_{298}	B3-LYP/A	0	0.6	1.4	10.5
	B3-LYP/B	0	—	1.2	11.4
ΔG_{298}	B3-LYP/A	0	−3.1	−0.8	8.8
	B3-LYP/B	0	—	−1.4	8.2

Table 4 The enthalpy and Gibbs energies differences (in kJ mol^{-1}) between the redox pairs trans-[W(CO)$_4$(η^2-C$_2$H$_4$)$_2$]$^{0/+}$ (**1**/**1**$^+$) and cis-[W(CO)$_4$(η^2-C$_2$H$_4$)$_2$]$^{0/+}$ (**2**/**2**$^+$)

	1/2			1$^+$/2$^+$
B3-LYP/A	B3-LYP/B	B3-LYP/A		B3-LYP/B
ΔH_{298}	14.2	15.3	−16.0	−13.0
ΔH_{213}	14.0	15.1	−15.9	−13.0
ΔG_{298}	10.0	11.9	−13.6	−9.8
ΔG_{213}	11.2	12.8	−14.3	−10.7

distance from tungsten (2.050 Å for B3-LYP/A and 2.056 Å for B3-LYP/B) than those in trans positions to the ethene ligands (1.993 and 2.000 Å with using A and B basis sets, respectively).

The DFT calculations indicate a thermodynamic instability of **2a** (C_2) relative to its trans-isomer **1** by about 10–12 kJ mol^{-1} (ΔG_{298}, Table 4). The calculated enthalpy difference (ΔH) is in a good agreement with ab initio calculations at the SCF level[22,23] that gave a value of 16.7 kJ mol^{-1}. Complete results of the thermochemical analysis of the trans and cis isomers of the neutral molecules and their cationic forms are given in the ESI.

[W(CO)$_5$(η^2-C$_2$H$_4$)] (3). The X-ray structure analysis of **3** (Fig. 3) shows the C=C bond eclipsed to one of the two equatorial OC–W–CO axes of the square-pyramidal W(CO)$_5$ unit, and perpendicular to the trans-located W–CO bond. This is in accordance with the results of a previous theoretical study of **3**[25,26] and our DFT data. Selected structural parameters for **3** are presented in Table 5. Complete data set for the calculated geometry is given in the ESI. The three different W–C(carbonyl) bond lengths have been calculated for **3**, two longer (in the equatorial plane) and one shorter (in an axial position). The two carbonyls staggered to the C=C bond lie slightly closer to tungsten (2.056 Å) than those eclipsed to the olefinic bond (2.062 Å), using the B3-LYP/B level of calculations. The structural parameters obtained here are in good agreement with the results of previous MP2 calculations (see Table 5).[26]
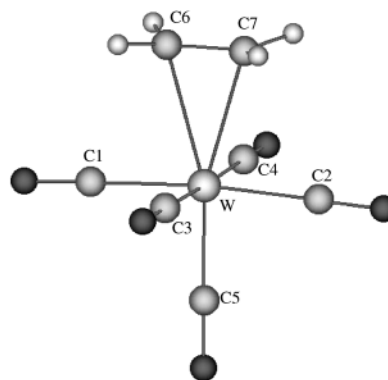
It is interesting to compare the W–C(ethene) and the C=C bond lengths in **1**, **2** and **3** calculated with the B3-LYP/B method. The W–C(ethene) distances to both carbon atoms in **1** are distinctly shorter (2.362 Å) than those in **2** (2.490 and 2.474 Å) and **3** (2.486 Å), while the C=C bond lengths show the opposite trend: **1** (1.411); **2** (1.380); and **3** (1.382 Å).

The mutually trans carbonyl ligands bind at nearly the same distance to the tungsten atom in alkene carbonyl compounds: **1** 2.055; **2** 2.056; and **3** 2.062 and 2.056 Å, eclipsed and staggered to the C=C bond, respectively.

Another significant diagnostic feature of these alkene carbonyl complexes is the W–CO bond length. For mutually trans

Fig. 3 Optimised geometry of [W(CO)$_5$(η^2-C$_2$H$_4$)] (**3**).

carbonyl ligands, the W–CO distances are larger (2.055 Å for **1**) than those for more firmly bound carbonyl ligands trans to ethene in **2** (2.000) and **3** (2.017 Å), consistent with the trans influence of the σ-donor and weaker π-acceptor alkene. As expected, analogous results were obtained using the B3-LYP/A method (Tables 1, 3 and 5).

trans- and cis-[W(CO)$_4$(η^2-C$_2$H$_4$)$_2$]$^+$ (1$^+$ and 2$^+$). Fig. 4 shows the optimised structures of the 17-electron cationic form of the trans and cis bis(ethene) compounds. Selected structural parameters are presented in Tables 1 and 3. The complete data sets are given in the ESI.

The calculations (B3-LYP/B) have shown that one-electron oxidation of compound **1** causes an increase in the W–C(ethene) distances by 0.121 Å (Table 1). The elongation of the W–C(carbonyl) bond is smaller (0.031 Å). Conversely, there is a slight shortening of the C=C bond length from 1.411 Å in **1** to 1.381 Å in **1**$^+$ (Table 1). Apparently, the single electron causes diminished d$_\pi$(W) π-back-donation to both CO and ethene ligands. In contrast to this, the one-electron oxidation of the cis-isomer **2** affects mainly the distance

**Table 3** Selected calculated structural parameters for the cis-[W(CO)$_4$(η^2-C$_2$H$_4$)$_2$]$^{0/+}$ complexes

Bond lengths and angles^a	cis-[W(CO)$_4$(η^2-C$_2$H$_4$)$_2$], **2a**		cis-[W(CO)$_4$(η^2-C$_2$H$_4$)$_2$]$^+$, **2**$^+$	
	B3-LYP/A	B3-LYP/B	B3-LYP/A	B3-LYP/B
W–C1; W–C2	1.993	2.000	2.074	2.079
W–C3; W–C4	2.050	2.056	2.064	2.070
W–C5; W–C8	2.479	2.490	2.460	2.477
W–C6; W–C7	2.466	2.474	2.460	2.477
C5–C6; C7–C8	1.387	1.380	1.387	1.379
C1–W–C2	90.91	91.98	86.95	88.30
C3–W–C4	172.31	172.72	176.69	176.78
W–C1–O1; W–C1–O1	179.74	179.55	179.79	179.27
W–C3–O3; W–C4–O4	178.24	178.55	179.47	179.62

^{a} Bond lengths are given in angstroms, bond angles in degrees.

Table 5 Selected experimental and calculated structural parameters for the $[W(CO)_5(\eta^2\text{-alkene})]$ complexes[a]

Alkene	Ref.	W–C(alkene)	W–CO Eclp.[b]	W–CO Stag.[c]	W–CO trans[d]	C=C	OC–W–CO Eclp[b]	OC–W–CO Stag[c]	W–C–O Eclp[b]	W–C–O Stag[c]	W–C–O trans[d]
C_2H_4	B3-LYP/A[e]	2.473	2.056	2.051	2.009	1.389	174.54	178.17	178.81	179.54	180.00
	B3-LYP/B[e]	2.486	2.062	2.056	2.017	1.382	174.95	176.90	179.10	179.68	180.00
	MP2[26]	2.372	2.054		2.026	1.402					
cis-C_8H_{14}	X-Ray[11]	2.49(1), 2.51(1)	2.02(1)	1.97(1)	1.96(1)	1.38(2)	173.4(4)	178.3(5)	178(1)	178(1)	179(1)
		2.01(1)		2.00(1)					177(1)	179(1)	
trans-C_8H_{14}	X-Ray[20]	2.425(4), 2.451(5)	2.031(4)	2.047(5)	2.011(5)	1.384(6)	175.4(2)	177.0(2)	178.4(4)	179.3(4)	176.5(4)
			2.050(5)	2.069(5)					178.1(4)	177.6(4)	

[a] Bond lengths are given in angstroms, bond angles in degrees. [b] W–CO bond eclipsed to C=C bond. [c] W–CO bond staggered to C=C bond. [d] W–CO bond *trans* to C=C bond. [e] This work.
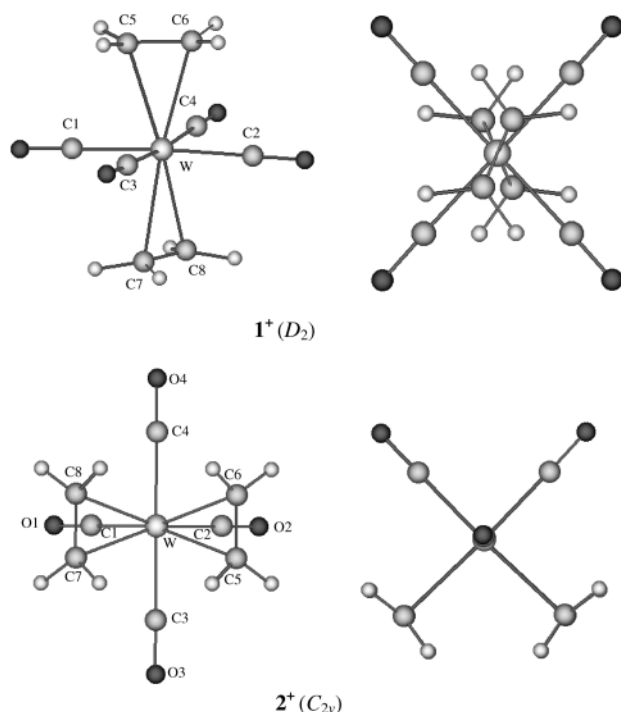
Fig. 4 Optimised geometries of formally 17-electron d[5] tungsten(I) complexes *trans*-$[W(CO)_4(\eta^2\text{-}C_2H_4)_2]^+$ (**1**[+]) and *cis*-$[W(CO)_4(\eta^2\text{-}C_2H_4)_2]^+$ (**2**[+]).

between tungsten and the carbonyl ligand in the *trans* position to the ethene ligand: 2.000 Å in **2** and 2.079 Å in **2**[+] (Table 3). The elongation of the W–C(carbonyl) distances for mutually *trans* carbonyl ligands in **2**[+] is smaller (0.014 Å). Also in this case, this phenomenon arises from diminished $d_\pi(W)$ to $\pi^*(CO)$ π-back-donation upon oxidation. However, the π-back-donation, diminished upon oxidation of **2**, is probably partly compensated for by increased σ-donation from the ethene ligands in **2**[+]. This explanation nicely agrees with the shorter W–C(ethene) distances in **2**[+] compared to those in parent compound **2** (Table 3) and with the higher stability of **2**[+] compared to **1**[+]. Indeed, there is an opposite energetic difference between the **1/2** and **1**[+]/**2**[+] redox pairs of isomers. The calculated potential energies indicate that 17-electron *cis* isomer **2**[+] is more stable than *trans* **1**[+] by about 14 or 10 kJ mol^{−1} (ΔG at B3-LYP/A or B3-LYP/B levels, respectively, Table 4).

IR characterisation of the alkene carbonyl complexes of tungsten

The calculated (B3-LYP/B, scaling factor of 0.9614[39]) and experimental $v(CO)$ vibration frequencies for **1**, **2** and **3** and

the corresponding 17-electron cations **1**[+] and **2**[+] are presented in Table 6. The comparison of the calculated and experimental $v(CO)$ wavenumbers and relative intensities show good agreement, in particular for the intense e mode of compound **1**.

The IR spectrum of compound **1** in *n*-hexane solution shows a characteristic $v(CO)$ pattern, with a very intense band at 1966 cm^{−1}, a weak one at 1990 cm^{−1} and a very weak one at 2058 cm^{−1}. These spectral features are fully consistent with the pseudo-octahedral geometry and D_{2d} symmetry[18] of **1** (Table 6). Two additional very weak $v(CO)$ bands at 1928 and 1917 cm^{−1} are observed in solution. In an argon matrix at *ca.* 14 K only one band was detected in this region at 1937 cm^{−1}. It has been assigned to the isotopomer *trans*-$[W(^{12}CO)_3(^{13}CO)(\eta^2\text{-}C_2H_4)_2]$.[18]

The *cis* isomer of $[W(CO)_4(\eta^2\text{-alkene})_2]$ was first spotted by IR spectroscopy as a thermally unstable product formed during the photolysis of $[W(CO)_6]$ in the presence of C_3H_6 in a rigid alkane glass at 77 K.[3] Compound **2** was identified as a photoproduct of $[W(CO)_6]$ in ethene-doped LXe solution at 195 K.[4] Furthermore, it has been proven that *cis*-bis(alkene) complexes also result from the photochemical isomerisation of *trans*-$[W(CO)_4(\eta^2\text{-alkene})_2]$ compounds at low temperatures.[16] Assignment of the *cis* geometry was based on their IR spectra, which exhibit four CO stretching bands, as expected from the C_2 symmetry of **2** (Table 6). For *cis*-$[W(CO)_4(\eta^2\text{-}C_2H_4)_2]$(**2**) in LXe at 195 K,[4] three $v(CO)$ bands were detected at 2050, 1957 (probably two unresolved bands) and 1910 cm^{−1}, while only two of the four $v(CO)$ bands were observed[18] at 2050 and 1913 cm^{−1} in *n*-hexane at room temperature (the other two $v(CO)$ bands are obscured by absorptions associated with the *trans* isomer **1**). A comparison of the calculated and observed $v(CO)$ frequencies for **2** reveals the largest difference (*ca.* 25 cm^{−1}) for the lowest energy b mode (vibration of the two CO groups *trans* to the ethene ligands). The data in Table 6 clearly shows the influence of solvent dipoles if we compare the position of the $v(CO)$ bands in the gas phase, *n*-hexane and CH_2Cl_2 solution.

It is generally accepted that predominantly metal-centred one-electron oxidation of metal carbonyls leads to an increased CO stretching frequency (Δv) by *ca.* 100 cm^{−1}.[21,42–45] This shift results from significantly reduced π-back-donation to the $\pi^*(CO)$ orbitals and strengthening of the C≡O bonds. A comparison of the predicted $v(CO)$ frequencies for the e mode of **1** and b$_2$ mode of **1**[+] gives a Δv value of 72 cm^{−1} (Table 6).

Upon one-electron oxidation of compound **2** the four $v(CO)$ bands shift to larger wavenumbers by 66, 84, 70 and 114 cm^{−1}, respectively. The order of the two b modes of **2** (1967 and 1938 cm^{−1}) is reversed in **2**[+]. The higher energy b mode for **2** (1967 cm^{−1}) and the b$_2$ mode for **2**[+] (2037 cm^{−1}) correspond to the vibration of the two mutually *trans* CO ligands. The lower energy b mode for **2** (1938 cm^{−1}) and the b$_1$ mode for **2**[+] (2052 cm^{−1}) are assigned to vibrations of the two CO ligands in *trans* positions to the alkene. The different Δv of 70 cm^{−1} for the two

Table 6 Calculated[a] and experimental freqencies (cm⁻¹) and intensities (in parentheses) for CO stretching bands of the studied alkene carbonyl complexes of tungsten

[W(CO)₆] (O_h)

a_{1g}	e_g	t_{1u}	Ref.	Medium
2109 (0) [b]	2019 (0) [b]	1996	This work	Gas phase
2126 (w)	2021 (vw)	1998 (vvs)	40	Gas phase

[W(CO)₅ (η²-C₂H₄)] (C_{2v})

a_1	a_1	B_2	a_1	b_1	Ref.	Medium
2077 (0.07)	2002 (0.001)	1981 (0.92)	1976 (0.43)	1967 (1)	This work	Gas phase
2083 (w)	—[c]	—[c]	1973 (s)	1955 (vs)	18	n-Hexane, 293 K

trans-[W(CO)₄(η²-C₂H₄)₂] (D_{2d})

a_1	b_2	e	¹³Co modes	Ref.	Medium
2055 (0)[c]	1996 (0.04)	1968 (1)		This work	Gas phase
2058 (vw)	1990 (w)	1966 (vs)	1928 (vw), 1917 (vw)	18	n-Hexane, 293 K
2053.9 (vw)	1999 (w)	1967.6 (vs)	1936.8 (vw)	18	Ar, 14 K
2058.6 (vw)	1989.8 (w)	1953.6 (vs)	1928 (vw), 1917 (vw)	This work[d]	n-Hexane, 233 K
2056 (w)	1986 (w)	1944 (vs)		This work[d]	CH₂Cl₂, 223 K

trans-[W(CO)₄(η²-C₂H₄)₂]⁺ (D_2)

a	b_1	b_3	b_2	Ref.	Medium
2114 (0)[c]	2051 (0.001)	2041 (0.88)	2040 (1)	This work	Gas phase

cis-[W(CO)₄(η²-C₂H₄)₂] (D_2)

a	a	b	b	Ref.	Medium
2042 (0.21)	1971 (0.27)	1967 (1)	1938 (0.66)	This work	Gas phase
2057.3 (w)	1957.5 (s)	1954.1 (s)	1897.2 (m)	18	Ar, 14 K
2050 (w)	—[c]	—[c]	1913 (m)	18	n-Hexane, 293 K
2050	1957	—[c]	1910	4	Xe, 195 K

cis-[W(CO)₄(η²-C₂H₄)₂]⁺ (D_2)

a_1	a_1	b_1	b_2	Ref.	Medium
2108 (0.25)	2055 (0.21)	2052 (0.48)	2037 (1)	This work	Gas phase
2127 (0.06)	2058 (0.41)	2035 (0.97)	2005 (1)	This work[d]	CH₂Cl₂, 223 K

[a] The scaling factor 0.9614[39] at the B3-LYP/B level was used. [b] IR inactive. [c] Not observed. [d] For [W(CO)₄(η²-C₄H₈)₂].

mutually *trans* CO ligands and Δv of 114 cm⁻¹ for the CO ligands *trans* to the alkenes correlate with the distinct effects of the one-electron oxidation of the tungsten centre on the W–CO bond distances. Calculated elongation of the W–CO bonds in **2** is indeed larger for carbonyls in positions *trans* to alkene ligands (0.079 Å) compared to that for the mutually *trans* carbonyl ligands (0.014 Å).

Oxidation-induced *trans–cis* isomerisation of lsqb;W(CO)₄-(η²-alkene)₂]

Isomerisation of Group 6 metal(0) carbonyls induced by electrochemical oxidation of the metal centre is a known phenomenon since the 1980's.[42–45] In the early 1990's oxidation of *trans*-[W(CO)₄(η²-alkene)₂] (alkene = 1-C₅H₁₀, 1-C₆H₁₂, C₅H₁₀, C₆H₁₀, C₇H₁₂ and C₈H₁₄) was also shown to produce the corresponding 17-electron cations in the *cis* configuration.[12] However, uncertainty has remained with regard to the mutual position of the W¹/W⁰ redox couples for the *trans*

and *cis* isomers. Herein, *trans*-[W(CO)₄(η²-1-butene)₂] (**1A**) has been chosen for a more detailed spectroelectrochemical study.

Cyclic voltammetry. The cyclic voltammogram of **1A** in dichloromethane shows a well-defined anodic wave at $E_{1/2} = +0.62$ V *vs.* Fc/Fc⁺ ($\Delta E_p = 90$ mV, comparable with 80 mV for Fc/Fc⁺ internal standard). At room temperature, the oxidation becomes a completely chemically reversible one-electron process at scan rates v higher than 1 V s⁻¹. For scan rates between 50–200 mV s⁻¹ a small cathodic peak is observed on reverse cathodic scanning at $E_p = -0.51$ V *vs.* Fc/Fc⁺ [Fig. 5(a)]. Its assignment to back-reduction of *cis*-[W(CO)₄(η²-1-butene)₂]⁺ (**2A⁺**) was facilitated by a thin-layer cyclic voltammogram recorded during the IR spectroelectrochemical experiment at 223 K [Fig. 5(b)].

There is no indication of electrocatalytic conversion of *trans*-[W(CO)₄(η²-1-butene)₂] (**1A**) upon oxidation to neutral *cis*-[W(CO)₄(η²-1-butene)₂] (**2A**). The latter *cis* isomer is thus oxidised less *positively* than the parent *trans* isomer **1A**.

(a)

E/mV vs Fc/Fc$^+$

(b)

1 Volt
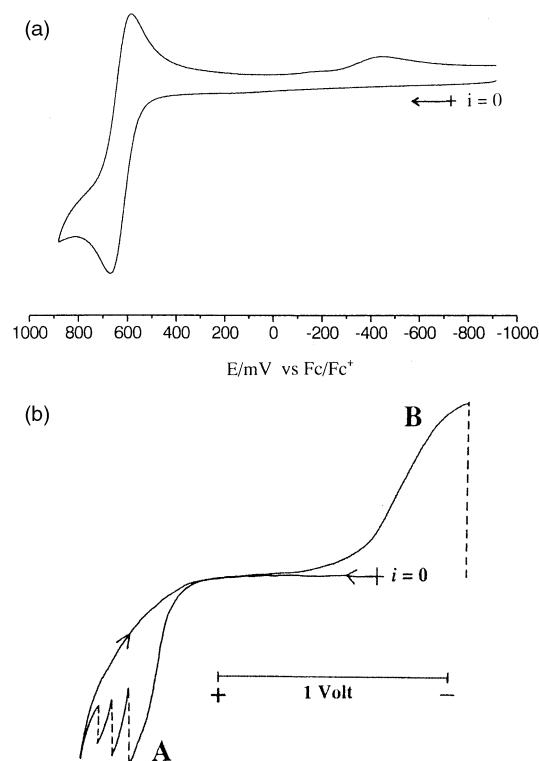
Fig. 5 (a) Cyclic voltammogram of *ca.* 10^{-3} M *trans*-[W(CO)$_4$(η^2-1-butene)$_2$] (**1A**) in CH$_2$Cl$_2$–0.1 M Bu$_4$NPF$_6$ at 293 K, $v = 200$ mV s^{-1}. (b) Thin-layer cyclic voltammogram of *ca.* 10^{-2} M complex **1A** in CH$_2$Cl$_2$–0.3 M Bu$_4$NPF$_6$ at 223 K, $v = 2$ mV s^{-1}, recorded during the IR spectroelectrochemical experiment depicted in Fig. 6. The dashed vertical lines indicate decreased current during electrolyses at constant potential. Anodic peak A: oxidation of **1A** producing **2A**$^+$; cathodic peak B: reverse reduction of **2A**$^+$ regenerating **1A**.

IR spectroelectrochemistry. IR v(CO) changes associated with the one-electron oxidation of **1A** were first studied in CH$_2$Cl$_2$ at 223 K within a low-temperature IR OTTLE cell [Fig. 5(b) and 6]. The v(CO) bands due to **1A** [2056 (w), 1986 (w-m) and 1944 (vs, br) cm^{-1}] were gradually replaced with a set of four new bands of a cationic carbonyl product at 2127 (w), 2058 (m), 2035 (s) and 2005 (s) cm^{-1} (Fig. 6).

The intensity pattern of the v(CO) bands is in agreement with C_{2v} symmetry the W(CO)$_4$ skeleton (Table 6). For the neutral *cis* isomer **2A**, only two out of the predicted four v(CO) bands (2041 and 1901 cm^{-1}) were observed[17] in *n*-hexane at 263 K. The IR spectrum of the electrochemically generated cation **2A**$^+$ with *cis* configuration shows the expected high frequency v(CO) shift. According to data in Table 6, an intense v(CO) band around 2030 cm^{-1} should be observed for the *trans* isomer **1A**$^+$ (2040 cm^{-1} predicted for the ethene derivative **1**$^+$). At this frequency, however, a strong band due to **2A**$^+$ also arose, thus a small quantity of the primary oxidation product **1A**$^+$ is hardly detectable by IR spectroscopy in a mixture with **2A**$^+$. However, no **1A**$^+$ was detected by thin-layer cyclic voltammetry in CH$_2$Cl$_2$ at 223 K upon reverse cathodic scanning beyond the anodic peak of parent **1** [Fig. 5(b)]. The only back-reduction occurred at an electrode potential of *ca.* -0.5 V *vs.* Fc/Fc$^+$; a potential difference larger than 1 V was observed between the oxidation of **1** and the reverse cathodic step. This observation proves exclusive formation of **2A**$^+$, which is sufficiently stable at 223 K. This result points to rapid oxidation-induced *trans–cis* isomerisation of **1A**$^+$ to **2A**$^+$, although **1A**$^+$ is still observable by cyclic voltammetry even at room temperature (see above). It is noteworthy that the back-reduction of **2A**$^+$ [Fig. 5(b)] resulted in direct complete recovery of the starting neutral *trans* isomer
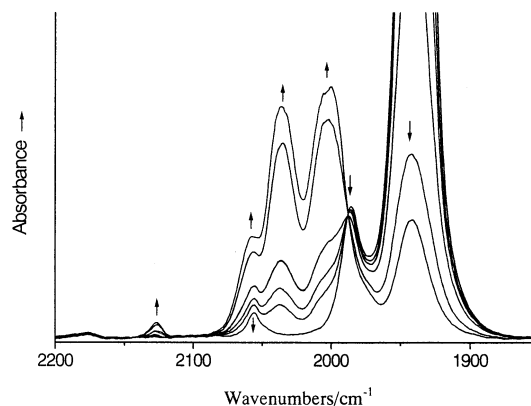
Fig. 6 IR spectral changes in the CO stretching region resulting from reversible one-electron oxidation of *ca.* 10^{-2} M *trans*-[W(CO)$_4$(η^2-1-butene)$_2$] (**1A**) in CH$_2$Cl$_2$ at 223 K within an OTTLE cell.[41]

1. The reverse reduction induced *cis–trans* isomerisation of **2A**$^+$ to **1** is therefore comparably fast.

The anodic IR spectroelectrochemical experiment performed at room temperature resulted in rapid decarbonylation, indicated by disappearance of the v(CO) absorption and evolution of CO gas at the anodic surface. Only a potential-step experiment and rapid oxidation of **1** within a few seconds led to a detectable weak v(CO) absorption due to the *cis* isomer **2A**$^+$. According to the cyclic voltammetric response, the primary *trans* isomer **1A**$^+$ is thermally unstable at room temperature on a subsecond time scale and could therefore hardly be detected in the course of the IR spectroelectrochemical oxidative experiment. Also this result supports assignment of the v(CO) bands at 2127 (w), 2058 (m), 2035 (s) and 2005 (s) cm^{-1} (Fig. 6) to **2A**$^+$. Thus, direct spectroscopic evidence for the existence of *cis*-[W(CO)$_4$(η^2-alkene)$_2$]$^+$ has now been obtained.

Conclusions

The results presented on the cyclic voltammetric and IR spectroelectrochemical studies at variable temperatures have unequivocally confirmed the identity of the formally 17-electron cationic species *cis*-[W(CO)$_4$(η^2-alkene)$_2$]$^+$ as the ultimate carbonyl product of the one-electron oxidation of *trans*-[W(CO)$_4$(η^2-alkene)$_2$]. Our theoretical results support the experimental data, showing that *trans*-[W(CO)$_4$(η^2-C$_2$H$_4$)$_2$] is more stable by about 10 kJ mol^{-1} (ΔG_{298}, B3-LYP/A) or 12 kJ mol^{-1} (ΔG_{298}, B3-LYP/B) than *cis*-[W(CO)$_4$(η^2-C$_2$H$_4$)$_2$], but stability of the cationic forms of these compounds is reversed; the cationic *cis* isomer is preferred by about 14 or 10 kJ mol^{-1} (ΔG_{298}, B3-LYP/A and B3-LYP/B, respectively).

References

1 I. W. Stolz, G. R. Dobson and R. K. Sheline, *Inorg. Chem.*, 1963, **2**, 1264.
2 F.-W. Grevels, M. Lindemann, R. Benn, R. Goddard and C. Kröger, *Z. Naturforsch., B: Anorg. Chem. Org. Chem.*, 1980, **35**, 1298.

3   K. R. Pope and M. S. Wrighton, *Inorg. Chem.*, **24**, 2792.
4   M. F. Gregory, S. A. Jackson, M. Poliakoff and J. J. Turner, *J. Chem. Soc., Chem. Commun.*, 1986, 1175.
5   S. A. Jackson, R. K. Upmacis, M. Poliakoff, J. J. Turner, J. K. Burdett and F.-W. Grevels, *J. Chem. Soc., Chem. Commun.*, 1987, 678.
6   F.-W. Grevels, J. Jacke and S. Özkar, *J. Am. Chem. Soc.*, 1987, **109**, 7536.
7   F.-W. Grevels, J. Jacke, P. Betz, C. Krüger and Y.-H. Tsay, *Organometallics*, 1989, **8**, 293.
8   G. Davidson and C. L. Davies, *Inorg. Chim. Acta*, 1989, **165**, 231.
9   S. A. Jackson, P. M. Hodges, M. Poliakoff, J. J. Turner and F.-W. Grevels, *J. Am. Chem. Soc.*, 1990, **112**, 1221.
10 P. M. Hodges, S. A. Jackson, J. Jacke, M. Poliakoff, J. J. Turner and F.-W. Grevels, *J. Am. Chem. Soc.*, 1990, **112**, 1234.
11 J. M. Dalla Riva Toma, P. H. Toma, P. E. Fanwick, D. E. Bergstrom and S. R. Byrn, *J. Crystallogr. Spectrosc. Res.*, 1993, **23**, 41.
12 M. Wilgocki, T. Szymańska-Buzar, M. Jaroszewski and J. J. Ziółkowski, in *Molecular Electrochemistry of Inorganic, Bioinorganic and Organometallic Compounds*, ed. A. J. L. Pombeiro and J. A. McCleverty, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1993, p. 573.
13 H. Takeda, M. Jyo-o, Y. Ishikawa and S. Arai, *J. Phys. Chem.*, 1995, **99**, 4558.
14 M. Jaroszewski, T. Szymańska-Buzar, M. Wilgocki and J. J. Ziółkowski, *J. Organomet. Chem.*, 1996, **509**, 19.
15 T. Szymańska-Buzar, M. Jaroszewski, W. Wilgocki and J. J. Ziółkowski, *J. Mol. Catal. A: Chem.*, 1996, **112**, 203.
16 T. Szymańska-Buzar, M. Jaroszewski, A. J. Downs, T. M. Greene and L. J. Morris, *J. Organomet. Chem.*, 1997, **531**, 207.
17 T. Szymańska-Buzar, K. Kern and D. J. Stufkens, *New J. Chem.*, 1998, **22**, 1539.
18 T. Szymańska-Buzar, K. Kern, A. J. Downs, T. M. Greene, L. J. Morris and S. Parsons, *New J. Chem.*, 1999, **23**, 407.
19 T. Szymańska-Buzar and K. Kern, *J. Organomet. Chem.*, 1999, **592**, 212.
20 F.-W. Grevels, J. Jacke, W. E. Klotzbücher, F. Mark, V. Skibbe, K. Schaffner, K. Angermund, C. Krüger, C. W. Lehmann and S. Özkar, *Organometallics*, 1999, **18**, 3278.
21 I. R. Farrell, F. Hartl, S. Záliš, M. Wanner, W. Kaim and A. Vlček, Jr., *Inorg. Chim. Acta*, 2001, **318**, 143.
22 C. Bachmann, J. Demuynck and A. Veillard, *J. Am. Chem. Soc.*, 1978, **100**, 2366.
23 C. Daniel and A. Veillard, *Nouv. J. Chim.*, 1986, **10**, 83.
24 C. Daniel and A. Veillard, *Inorg. Chem.*, 1989, **28**, 1170.
25 T. A. Albright, R. Hoffmann, J. C. Thibeault and D. L. Thorn, *J. Am. Chem. Soc.*, 1979, **101**, 3801.
26 U. Pidun and G. Frenking, *Organometallics*, 1995, **14**, 5325.
27 T. Szymańska-Buzar, *J. Mol. Catal.*, 1988, **48**, 43.
28 T. Szymańska-Buzar, *J. Mol. Catal. A: Chem.*, 2000, **160**, 133.
29 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, GAUSSIAN 98, rev. A.9, Gaussian, Inc., Pittsburgh PA, 1998.
30 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.
31 P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 299.
32 M. J. Frisch, E. Frisch and J. B. Foresman, *GAUSSIAN 94 Users Reference*, Gaussian, Inc., Pittsburgh PA, 1996.
33 R. Bauernschmitt and R. Ahlrichs, *J. Chem. Phys.*, 1996, **104**, 9047.
34 H. B. Schlegel, *J. Chem. Phys.*, 1982, **77**, 3676.
35 C. Peng, P. Y. Ayala, H. B. Schlegel and M. J. Frisch, *J. Comput. Chem.*, 1996, **17**, 49.
36 B. Jost and A. Rees, *Acta Crystallogr., Sect. B*, 1975, **31**, 2649.
37 J. Li, G. Schreckenbach and T. Ziegler, *J. Am. Chem. Soc.*, 1995, **117**, 486.
38 A. W. Ehlers, Y. Ruiz-Morales, E. J. Baerends and T. Ziegler, *Inorg. Chem.*, 1997, **36**, 5031.
39 A. P. Scott and L. Radom, *J. Phys. Chem.*, 1996, **100**, 16 502.
40 L. H. Jones, R. S. McDowell and M. Goldblatt, *Inorg. Chem.*, 1969, **8**, 2349.
41 F. Hartl, H. Luyten, H. A. Nieuwenhuis and G. C. Schoemaker, *Appl. Spectrosc.*, 1994, **48**, 1522.
42 A. M. Bond and R. Colton, *Coord. Chem. Rev.*, 1997, **166**, 181. and references therein.
43 S. Sun and D. A. Sweigart, *Adv. Organomet. Chem.*, 1997, **40**, 171. and references therein.
44 K. A. Conner and R. A. Walton, *Organometallics*, 1983, **2**, 169.
45 R. D. Rieke, H. Kojima, T. Saji, P. Rechberger and K. Öfele, *Organometallics*, 1988, **7**, 749.