Isomeric Olefin Tetracarbonyl Complexes of Tungsten(I): An Infrared Spectroelectrochemical Study at Low Temperatures

Marcin Górski,[†] František Hartl,[‡] and Teresa Szymańska-Buzar*,[†]

Faculty of Chemistry, University of Wrocław, ul. F. Joliot-Curie 14, 50-383 Wrocław, Poland, and Homogeneous and Supramolecular Catalysis, Van't Hoff Institute for Molecular Sciences, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

In situ electrolysis within an optically transparent thin-layer electrochemical (OTTLE) cell was applied at 293−243 K in combination with FTIR spectroscopy to monitor spectral changes in the carbonyl stretching region accompanying oxidation of four tetracarbonyl olefin complexes of tungsten(0), viz., *trans*-[$W(CO)_4(\eta^2$-ethene$)_2$], *trans*-[$W(CO)_4(\eta^2$-norbornene$)_2$], [$W(CO)_4(\eta^4$-cycloocta-1,5-diene)], and [$W(CO)_4(\eta^4$-norbornadiene)]. In all cases, the one-electron-oxidized radical cations (17-electron complexes) have been identified by their characteristic ν(C≡O) patterns. For the bidentate diene ligands, the *cis* stereochemistry is essentially fixed in both the 18- and 17-electron complexes. The radical cation of the *trans*-bis(ethene) complex was observed only at 243 K, while at room temperature it isomerized rapidly to the corresponding *cis*-isomer. The thermal stability of the three studied radical cations in the *cis* configuration correlates with the relative strength of the W−CO bonds in the positions *trans* to the olefin ligand, which are more affected by the oxidation than the axial W−CO bonds. For the bulky norbornene ligands, their *trans* configuration in the bis(norbornene) complex remains preserved after the oxidation in the whole temperature range studied. The limited thermal stability of the radical cations of the *trans*-bis(alkene) complexes is ascribed to dissociation of the alkene ligands. The spectroelectrochemical results are in very good agreement with data obtained earlier by DFT (B3LYP) calculations.

Introduction

The chemistry of group 6 metal penta- and tetracarbonyl complexes with olefin ligands has been widely examined since their initial IR spectroscopic characterization by Stolz et al. in 1963.[1] On the contrary, their redox behavior has remained largely unexplored.[2] A particularly intriguing topic in the area of redox activation is the electron-transfer-induced geometrical isomerization of di- and trisubstituted pseudooctahedral carbonyl complexes.[3,4] In a brief report from 1993, Wilgocki et al.

mentioned the occurrence of oxidative *trans* → *cis* isomerization also for several bis(alkene) tetracarbonyl complexes of tungsten-(0), though without convincing spectroelectrochemical evidence.[5] The closed-shell neutral bis(alkene) tetracarbonyl complexes can exist in two geometrical forms (*trans* and *cis*), of which only the thermodynamically more stable *trans*-isomers have been isolated so far.[2] The labile *cis*-bis(alkene) isomers, usually detectable as products of photolysis at low temperatures, have nevertheless been supposed to be active species in homogeneous catalysis with group 6 transition metal carbonyl complexes.[2] In the particular case of tungsten(0) complexes under study in our laboratories, attention should be paid to the role of electron transfer in their transformation to catalytically active species, following the principles of electron-transfer chain catalysis in organotransition metal chemistry.[6−8] Combined experimental and theoretical efforts are highly desirable to explain and predict structural changes and to obtain deeper mechanistic insights. For example, density functional theory (DFT) calculations indicate that the 17-electron tungsten(I) complex *cis*-[$W(CO)_4(\eta^2$-ethene$)_2$]$^+$ is ca. 10 kJ mol^{-1} more stable than its *trans*-isomer.[9] On the other hand, DFT calculations point to facile stepwise transformation of the corresponding

* Corresponding author. E-mail: tsz@wchuwr.chem.uni.wroc.pl. Fax: +48 71 328 23 48. Tel: +48 71 375 7221.

† University of Wrocław.

‡ University of Amsterdam.

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Chart 1 Schematic Molecular Structures of Studied Olefin Complexes 1−4
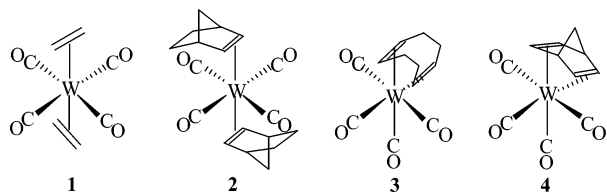
Table 1. Cyclic Voltammetric Data for Complexes 1−4[a]

compd	$E_{1/2}^{ox}$ (V)	$E_{p,a} - E_{p,c}$ (mV)
1	0.73	90
2	0.42	80
3	0.53	80
4	0.56[b]	−[b]

[a] Conditions: 10^{-3} M complex in dichloromethane containing 10^{-1} M Bu$_4$NPF$_6$; $\nu = 100$ mV s^{-1}; $T = 293$ K; Pt disk microelectrode. [b] $E_{p,a}$ value for irreversible oxidation. $E_{p,a} - E_{p,c} = 80$ mV for the cobaltocene/cobaltocenium internal standard.

dicationic tungsten(II) complex to tungstacyclopentane and butylidene species active in catalytic olefin metathesis.[2]

In the course of our exploration of olefin rearrangement in the coordination sphere of tungsten carbonyls, we have focused on the processes induced by electrochemical oxidation of the metal center. We have been interested in the influence of the olefin nature on the oxidation potentials of the parent complexes and stability of the electron-deficient cationic products. In the present infrared spectroelectrochemical study, we describe one-electron oxidation of four selected tungsten(0) tetracarbonyl bis-(alkene) and diene complexes with *trans* and *cis* mutual positions of the W-(η^2-C=C) bonds, respectively (Chart 1). The neutral complexes with chelating diene ligands served as convenient models for the nonaccessible *cis*-isomers of the bis-(alkene) tetracarbonyls.

Results and Discussion

Electrochemistry. Cyclic voltammetric study of the four studied olefin complexes (Chart 1) was carried out in dichloromethane. The results are summarized in Table 1.

At room temperature, the cyclic voltammograms of the bis-(norbornene) (*trans*-**2**) and cyclooctadiene (**3**) complexes show a fully reversible anodic wave even at the limiting scan of 0.02 V s^{-1}. Comparison with the standard ferrocene/ferrocenium and/or cobaltocenium/cobaltocene redox couples used as internal references confirms diffusion control of the electron transfer. On the other hand, oxidation of bis(ethene) complex *trans*-**1** becomes reversible only at $\nu \geq 2$ V s^{-1}. At slower scans, the cathodic-to-anodic peak current ratio, $I_{p,c}/I_{p,a}$ drops below 1, viz., 0.96 at 1 V s^{-1}, 0.93 at 0.5 V s^{-1}, and 0.84 at 0.1 V s^{-1}. With the decreasing scan rate, a new cathodic waves grows on the reverse scan at $E_{p,c} = 0.05$ V vs Fc/Fc$^+$ (Figure 1). Fully reversible oxidation of complex **1** was also achieved at temperatures below 0 °C.

In contrast to complexes *trans*-**1**, *trans*-**2**, and **3**, the anodic response of norbornadiene complex **4** is totally irreversible at room temperature (Figure 2), in agreement with an earlier report by Kochi et al.[10] No change in this behavior was observed even at 205 K. The absence of the corresponding cathodic counter-peak implies a rapid chemical transformation of the 17e product **4**$^+$, which was also confirmed by infrared spectroelectrochemical

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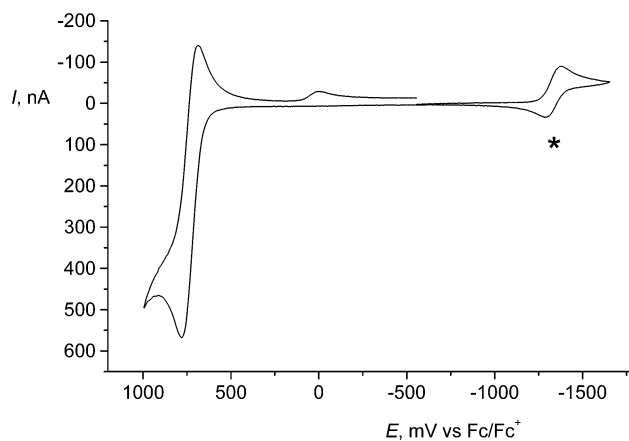
Figure 1. Cyclic voltammogram of *trans*-[W(CO)$_4$(η^2-ethene)$_2$] (**1**) in dichloromethane. The redox couple at −1.33 V, denoted by an asterisk, is the cobaltocene/cobaltocenium internal reference. Conditions: Pt disk microelectrode, $\nu = 100$ mV s^{-1}, room temperature.
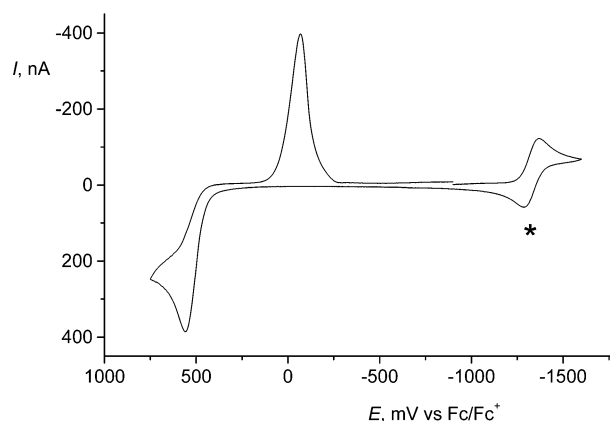
Figure 2. Cyclic voltammogram of [W(CO)$_4$(η^4-norbornadiene)$_2$] (**4**) in dichloromethane. The redox couple at −1.33 V, denoted by an asterisk, is the cobaltocene/cobaltocenium internal reference. Conditions: Pt disk microelectrode, $\nu = 100$ mV s^{-1}, room temperature.

monitoring (see below). A new cathodic peak appeared during the reverse cathodic sweep at −0.07 V (at room temperature), which is comparable with the cyclic voltammogram of complex **1**. In this case, however, the reduction of the secondary anodic product is strongly affected by its adsorption at the polished Pt disk microelectrode (Figure 2). It is noteworthy that the internal reference, the cobaltocenium/cobaltocene redox couple, re-mained unaffected by the irreversible voltammetric response of complex *trans*-**1**, as testified by $\Delta E_p = 80$ mV at $\nu = 0.1$ V s^{-1}.

Norbornadiene complex **4** and cycloocta-1,5-diene complex **3** with the *cis* arrangement of the W−(η^2-C=C) bonds oxidize at similar anodic potentials around 0.56 V vs Fc/Fc$^+$ (Table 1). The reversible oxidation of bis(norbornene) complex *trans*-**2** lies at a slightly lower anodic potential, viz., 0.46 V, while for bis(ethene) complex *trans*-**1** the anodic wave has a distinctly higher potential, viz., 0.73 V. The more difficult oxidation of *trans*-**1** is probably a result of higher π-acceptor ability of the coordinated ethene compared to the other olefin ligands. This explanation is further supported by the higher CO-stretching frequencies of complex *trans*-**1** than those obtained for complexes *trans*-**2**, **3**, and **4** (Table 2). In addition, the W−C(ethene) bond in complex *trans*-**1**, determined by X-ray diffraction analysis, is ca. 0.1 Å shorter compared to W−C(diene) bond lengths in complexes **3** and **4** and slightly shorter than reported

Table 2. Infrared Spectral Data for Complexes 1−4 and Products of Their One-Electron Oxidation[a]

compd	T (K)	$\nu(C\equiv O)$ (cm^{-1})
trans-**1**	293	2062 (vw), 1994 (vw), 1956 (vs)
trans-**1**	243	2061 (vw), 1992 (vw), 1955 (vs)
trans-**1**[b]		2055 (0), 1996 (0.04), 1968 (1)
trans-**1**[+]	243	2131 (vw), 2066 (sh, m-w), 2042 (s), 2014 (vs)
trans-**1**[+b]		2114 (0), 2051 (0.001), 2041 (0.88), 2040 (1)
cis-**1**[b]		2042 (0.21), 1971 (0.27), 1967 (1), 1938 (0.66)
cis-**1**[+]	293	2125 (m), 2055 (sh), 2035 (vs)
cis-**1**[+b]		2108 (0.25), 2055 (0.21), 2052 (0.48), 2037 (1)
trans-**2**	293	2041 (vw), 1974 (w), 1928 (vs)
trans-**2**	243	2040 (vw), 1972 (w), 1926 (vs)
trans-**2**[+]	293	2111 (vw), 2045 (w), 2013 (vs)
trans-**2**[+]	243	2110 (vw), 2042 (w), 2014 (vs)
3	293	2036 (m), 1942 (vs, br), 1879 (s)
3	243	2034 (m), 1941 (vs, br), 1871 (s)
3[+]	293	2110 (m), 2046 (m,br), 2013 (vs)
3[+]	243	2110 (m), 2046 (m,br), 2010 (vs)
4	293	2036 (m), 1941 (vs, br), 1878 (s)
4	243	2034 (m), 1940 (vs, br), 1870 (s)
4[+]	243	2112 (m), 2064 (m), 2036(sh), 2018 (s)

[a] All experimental IR spectra were recorded in dichloromethane containing 2.5×10^{-1} M Bu$_4$NPF$_6$. [b] DFT data reported by Handzlik et al. in ref 9; relative band intensities are given in parentheses.
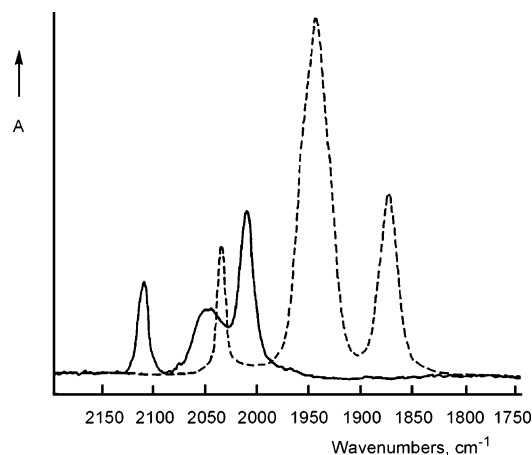
Figure 3. IR spectra of [W(CO)$_4$(η^4-cycloocta-1,5-diene)] (**3**) (dashed line) and 1*e*-oxidized **3**[+] (full line). Conditions: oxidation of **3** within an OTTLE cell in dichloromethane at 243 K.

for the closely related *trans*-bis(cyclooctene) tungsten(0) tetracarbonyl.[2,11−14]

Infrared Spectroelectrochemistry. Infrared spectra of the diene tungsten(0) complexes **3** and **4** with the *cis* arrangement of the W−(η^2-C=C) bonds (local C_{2v} symmetry[2]) exhibit three $\nu(C\equiv O)$ bands in the range 2040−1870 cm^{-1} (Table 2), the middle one with a shoulder on the high-frequency side. These absorption bands correspond to a$_1^{(1)}$, close-lying a$_1^{(2)}$ + b$_1$, and b$_2$ stretching modes, all being IR-active. Monitoring the fully reversible 1*e* oxidation of cycloocta-1,5-diene complex **3** carried out in the OTTLE cell at 243 K has revealed a large high-frequency shift of the $\nu(C\equiv O)$ bands (Figure 3). The shift magnitude (>70 cm^{-1}) corresponds to predominantly tungsten-localized W(0) → W(I) oxidation and greatly diminished W → CO π-back-donation. A very similar result has been obtained at room temperature (Table 2), in agreement with the inherent

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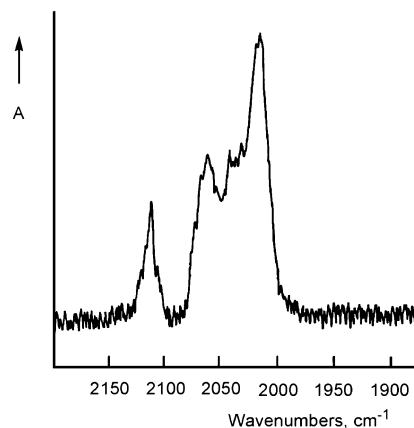
Figure 4. IR spectrum of [W(CO)$_4$(η^4-norbornadiene)]$^+$ (**4**[+]). Conditions: 1*e* oxidation of parent complex **4** within an OTTLE cell in dichloromethane at 243 K.

stability of **3**[+]. The intensities of the $\nu(C\equiv O)$ bands of **3**[+] are much lower than those of precursor **3**, which applies also to the other studied W(0) and W(I) complexes (see below). It is noteworthy that the broad middle band has a fairly low intensity in the IR spectrum of **3**[+], while it is dominant in the IR spectrum of **3**. The observed high intensity of the lowest-energy $\nu(C\equiv O)$ band in **3**[+] has correctly been predicted by DFT (B3LYP) calculations[9] on related bis(ethene) cation *cis*-**3**[+]. The calculations have revealed that the intense b$_1$ and weaker b$_2$ absorptions in *cis*-**1** interchange their energetic positions in *cis*-**1**[+] (two b modes, local C_2 symmetry[2]), which probably accounts also for the different $\nu(C\equiv O)$ intensity patterns of complexes **3** and **3**[+] (Figure 3).

The irreversible oxidation of norbornadiene complex **4**, as observed by cyclic voltammetry (see above), gave hardly any chance to characterize **4**[+] by IR spectroscopy. Indeed, at room temperature no carbonyl product was detected during the anodic electrolysis of **4**. The decarbonylation of **4**[+] was also evidenced by CO gas development at the anode. The presence of free CO in the solution was indicated by a weak absorption at ca. 2140 cm^{-1}.[15] Surprisingly, when the oxidation of complex **4** in the thin solution layer was performed at 243 K in a potential step, we observed a small amount of **4**[+] (Figure 4). The assignment has been based on comparison with the IR spectrum of the stable W(I) radical cation **3**[+], the latter showing similar $\nu(C\equiv O)$ wavenumbers and intensity pattern with the broad middle absorption band at 2046 cm^{-1}. This absorption is resolved in the case of **4**[+] into two bands of medium intensities and a very close average wavenumber value (Table 2).

A similar large shift to higher $\nu(C\equiv O)$ frequencies was observed in the IR spectra recorded during the W(0) → W(I) oxidation of the bis(norbornene) complex *trans*-**2** (Table 2). The neutral parent complex exhibits a very intense $\nu(C\equiv O)$ band at 1926 cm^{-1} (243 K), corresponding to the e mode in the local D_{2d} symmetry,[2] if only the carbonyl groups are considered (Figure 5). The weak bands of *trans*-**2** at 2040 and 1972 cm^{-1} represent a$_1$ and b$_2$ vibrational modes, respectively.[9] It is important to stress the very low-intensity a$_1$ mode (IR-inactive in D_{2d}), which is characteristic for *trans*-[W(CO)$_4$(η^2-alkene)$_2$] complexes. In contrast, a medium intensity of the symmetric all-carbonyl stretch (IR-active a$_1^{(1)}$ mode) was observed for complexes **3** and **4** with the *cis* arrangement (Figures 3 and 4), which also agrees with the DFT (B3LYP) data calculated[9] for the *trans*-**1** and *cis*-**1** isomers. The oxidation of complex *trans*-**2**

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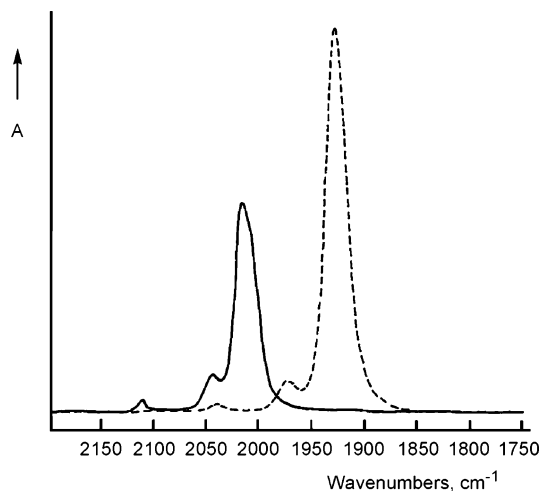
Figure 5. IR spectra of *trans*-[W(CO)$_4$(η^2-norbornene)$_2$] (**2**) (dashed line) and 1*e*-oxidized **2**$^+$ (full line). Conditions: oxidation of **2** within an OTTLE cell in dichloromethane at 243 K.
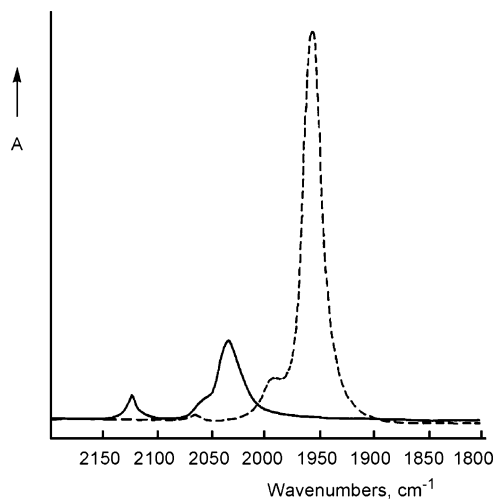
Figure 6. IR spectra of *trans*-[W(CO)$_4$(η^2-ethene)$_2$] (*trans*-**1**) (dashed line) and 1*e*-oxidized *cis*-[W(CO)$_4$(η^2-ethene)$_2$]$^+$ (*cis*-**1**$^+$) (full line). Conditions: oxidation of *trans*-**1** and concomitant isomerization of *trans*-**1**$^+$ within an OTTLE cell in dichloromethane at 293 K.

to *trans*-**2**$^+$ was fully reversible at 243 K. The radical cationic product exhibits the same ν(C≡O) band intensity pattern (Figure 5), thereby excluding any *trans* → *cis* isomerization induced by the electron transfer. Again, the *trans* arrangement of the norbornene ligands in *trans*-**2**$^+$ has been supported by the very low intensity of the ν(C≡O) band at 2110 cm^{-1} (Raman-active a mode, D_2 local symmetry), in line with the DFT calculations[9] on the closely related cation *trans*-**1**$^+$ (Table 2). At room temperature, primary oxidation product *trans*-**2**$^+$ lives only a few minutes and could be detected by IR spectroscopy shortly after a rapid potential step. Again, no *trans* → *cis* isomerization was observed.

In marked contrast to bis(norbornene) complex *trans*-**2**, IR spectroelectrochemical monitoring of one-electron oxidation of bis(ethene) derivative *trans*-**1** revealed a more complex behavior. The IR spectrum of the fairly stable product obtained upon oxidation of *trans*-**1** at room temperature displays one strong band at 2035 cm^{-1} with a shoulder at ca. 2055 cm^{-1} and, importantly, a medium-intensity band at 2125 cm^{-1} (Figure 6). It resembles the IR spectrum of cycloocta-1,5-diene cation **3**$^+$
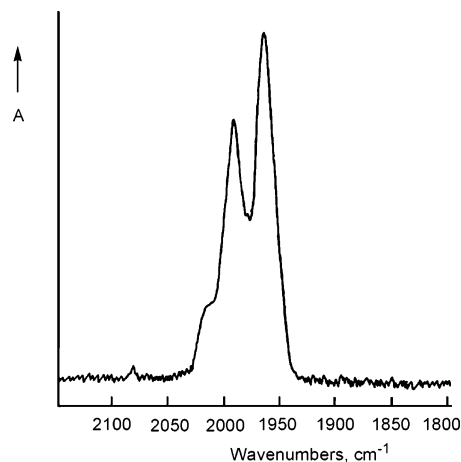
Figure 7. IR spectrum of *trans*-[W(CO)$_4$(η^2-ethene)$_2$]$^+$ (*trans*-**1**$^+$). Conditions: 1*e* oxidation of parent complex *trans*-**1** within an OTTLE cell in dichloromethane at 243 K.

(Figure 3) with the carbonyl ligands in two different configurations, (i) mutually *trans* and (ii) *trans* to the diene C═C bonds. This comparison points to fast *trans* → *cis* isomerization of *trans*-**1**$^+$ following the one-electron oxidation of *trans*-**1**. From preceding DFT (B3LYP) calculations[9] it is known that the *cis*-bis(ethene) cationic complex (*cis*-**1**$^+$) is thermodynamically more stable by ca. 10 kJ mol^{-1} than *trans*-**1**$^+$. The four computed ν(C≡O) frequencies and relative intensities (in parentheses) of *cis*-**4**$^+$ are 2108 (0.25), 2055 (0.21), 2052 (0.48), and 2037 (1) cm^{-1}.[9] The DFT data thus reproduce very well the experimental IR spectrum.

According to the reversible cyclic voltammetric response of *trans*-**1** (see above), lowering the temperature of the OTTLE cell was expected to facilitate IR spectroscopic detection of the initially formed cation *trans*-**1**$^+$. Figure 7 shows ν(C≡O) bands in the IR spectrum recorded at 243 K, with frequencies and intensities that indeed significantly differ from the band pattern obtained at room temperature: 2131 (vw), 2066 (sh, m-w), 2042 (s), 2014 (vs) cm^{-1}. This experimental result agrees appreciably with the DFT data computed for *trans*-**1**$^+$ (the intensities are given in parentheses): 2114 (0), 2051 (0.001), 2041 (0.88), and 2040 (1) cm^{-1}. In the experimental spectrum, the two intense bands at 2042 and 2014 cm^{-1} probably correspond to the low-energy b$_3$ and b$_2$ modes with nearly identical theoretical[9] wavenumbers, reminiscent of the single e mode in parent complex *trans*-**1**. Cation *trans*-**1**$^+$ differs in this respect from *trans*-**2**$^+$ (Figure 5) but resembles another W(I) tetracarbonyl with linear alkene ligands, viz., *trans*-[W(CO)$_4$(η^2-but-1-ene)$_2$]$^+$ (ν(C≡O) at 2127 (vw), 2058 (sh, m), 2035 (vs), and 2005 (vs) cm^{-1}.[16] The latter radical complex is fully stable at 223 K, like *trans*-**2**$^+$. In contrast, oxidation of *trans*-**1** at 243 K produces also [W(CO)$_6$] (ν(C≡O) at 1975 cm^{-1}; omitted in Figure 7), indicating dissociation of the ethene ligands, the weakest σ-donors in the series (Table 2). This behavior is explained below.

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(16) The cationic complex [W(CO)$_4$(η^2-but-1-ene)$_2$]$^+$ was originally described as the *cis*-isomer, on the basis of the separation of all four CO-stretching modes and a large ΔE_p value from slow-scan thin-layer cyclic voltammetry.[9] However, the comprehensive results presented in this work for complexes **1**–**4**, in particular the characteristic very low intensity of the IR-forbidden highest-frequency all-CO stretch for *trans*-[W(CO)$_4$(η^2-alkene)$_2$]$^{0/+}$ and the absence of *trans* → *cis* isomerization for cation *trans*-**2**$^+$ above 243 K, have prompted us to rectify the assignment of the cationic oxidation product as *trans*-[W(CO)$_4$(η^2-but-1-ene)$_2$]$^+$. The latter species decomposes at room temperature but does not isomerize, similar to *trans*-**2**$^+$.

As calculated earlier,[9] the four $\nu(C\equiv O)$ bands of bis(ethene) complex *cis*-**1** ($a_1^{(1)}$, $a_1^{(2)}$, b_1, and b_2 modes) shift upon the one-electron oxidation to higher frequencies by 66, 84, 70, and 114 cm^{-1}, respectively. The vibration of the two CO ligands in *trans* positions to the ethene ligands corresponds to the b mode at 2052 cm^{-1} in *cis*-**1**$^+$ (C_2 symmetry) and to the b_2 mode at 1938 cm^{-1} in neutral complex *cis*-**1** (C_{2v} symmetry). The energetic separation between these two modes, $\Delta\nu = 114$ cm^{-1} for *cis*-**1**/*cis*-**1**$^+$, increases significantly to 175 cm^{-1} and 194 cm^{-1} for the couples **3**/**3**$^+$ and **4**/**4**$^+$. On the other hand, much smaller wavenumber differences have been determined for vibrations of two mutually *trans* carbonyl ligands in the redox couples *trans*-**1**/*trans*-**1**$^+$ ($\Delta\nu = 59$ cm^{-1}) and *trans*-**2**/*trans*-**2**$^+$ ($\Delta\nu = 88$ cm^{-1}). From the comparison of these $\Delta\nu$ values it is clear that the one-electron oxidation of a tetracarbonyl W(0) complex containing two mutually *cis*-arranged olefin ligands removes the electron density to a higher extent from π-orbitals representing the W−CO bonds *trans* to the W−olefin bonds than from the W−CO π-bond of the mutually *trans* carbonyl ligands. For this reason, the lability of the carbonyl ligands in the oxidized complexes should correlate with the $\Delta\nu$ value increasing in the order *cis*-**1**$^+$ < **3**$^+$ < **4**$^+$. This reasoning may partly explain the observed high reactivity of the 17*e* complex with chelating norbornadiene (**4**$^+$) compared with the fairly high stability of the cationic bis(ethene) complex *cis*-**1**$^+$. The decarbonylation of **4**$^+$ (detectable in situ at 243 K) was indeed confirmed by IR spectroscopic monitoring.

The $\Delta\nu$ separation of the e mode of *trans*-**1** (D_{2d}) and the b_2 mode of *trans*-**1**$^+$ (D_2), both corresponding to vibrations of the two mutually *trans* CO ligands, amounts 59 cm^{-1} (243 K). This value is thus much smaller than those characterizing the vibration of the CO ligands in *trans* positions to the olefin ligands in complexes *cis*-**1**, **3**, and **4** and their 1*e*-oxidized forms (see above). These data suggest that the one-electron oxidation of bis(olefin) complexes *trans*-**1** and *trans*-**2** removes the electron density mainly from the π-orbitals of the tungsten−olefin bonds, inducing dissociation of the olefin ligands. This behavior corresponds nicely with the formation of $[W(CO)_6]$ in the course of the oxidation of complex *trans*-**1** at 243 K, where no *trans* → *cis* isomerization takes place. For the redox couple *trans*-**2**/*trans*-**2**$^+$, the larger $\Delta\nu$ value of 88 cm^{-1} for the e and b_2 modes, respectively, is fully in line with the higher stability of *trans*-**2**$^+$ compared to *trans*-**1**$^+$. Norbornene is also a stronger σ-donor than ethene, as testified by the smaller ν-($C\equiv O$) wavenumbers of *trans*-**2** compared to those of *trans*-**4** (Table 2), capable of better stabilizing the W(I) oxidation state. At the same time, the greater steric demands of the mutually *cis*-arranged norbornene ligands in hypothetical *cis*-**2**$^+$ compared to the smaller ethene in *cis*-**1**$^+$ can be considered as a plausible explanation for the completely hindered *trans* → *cis* isomerization of 1*e*-oxidized *trans*-**2**$^+$.

Conclusions

These results document that infrared thin-layer spectroelectrochemistry at variable temperatures is a valuable tool to study the anodic processes in tungsten(0) carbonyls with olefin and diene ligands in different (*trans* and *cis*) arrangements.

The IR spectroscopic data show that the one-electron oxidation of the neutral parent complexes can be generally assigned as W(0) → W(I). However, the magnitude of the high-frequency $\nu(C\equiv O)$ shifts depends on the mutual positions of the carbonyl and olefin ligands, suggesting that significant electron density is removed from different W−olefin and W−carbonyl π-orbitals. In particular, the one-electron oxidation of a tetracarbonyl

cis-isomer affects mainly the W−CO bonds *trans* to the W−olefin bonds. The lability of these carbonyl ligands ought to be higher in 17-electron diene complexes **3**$^+$ and **4**$^+$ than the carbonyls in bis(alkene) complexes *trans*-**1**$^+$ and *trans*-**2**$^+$. The comparison of the $\Delta\nu(C\equiv O)$ shifts has further revealed that in the latter two cations the oxidation mainly weakened the W−alkene bonds. The analysis of the bonding situation is consistent with the facile decarbonylation of **4**$^+$ even at low temperatures and observation of $[W(CO)_6]$ in the IR spectra of *trans*-**1**$^+$.

At room temperature, cation *trans*-**1**$^+$ undergoes spontaneous *trans* → *cis* isomerization, in agreement with higher thermodynamic stability of *cis*-**1**$^+$ as computed by DFT. The absence of *trans* → *cis* isomerization for *trans*-**2**$^+$ has been tentatively ascribed to steric hindrance of the bulky norbornene ligands in mutual *cis* positions.

Experimental Section

General Procedures. Standard inert-atmosphere techniques were used for all syntheses and sample manipulations. Dichloromethane (Acros; analytical quality) was dried over P_2O_5 and freshly distilled under nitrogen. The supporting electrolyte Bu$_4$NPF$_6$ (Aldrich) was recrystallized twice from absolute ethanol and dried overnight under vacuum at ca. 80 °C. $[W(CO)]_6$ (Merck) was used as received. Olefins (Sigma-Aldrich) were dried over CaH$_2$ and distilled under nitrogen prior to use.

Syntheses. The preparation of the studied olefin complexes (Chart 1) *trans*-$[W(CO)_4(\eta^2\text{-ethene})_2]$ (*trans*-**1**),[11] *trans*-$[W(CO)_4$-$(\eta^2\text{-norbornene})_2]$ (*trans*-**2**),[18] $[W(CO)_4(\eta^4\text{-cycloocta-1,5-diene})]$ (**3**),[17] and $[W(CO)_4(\eta^4\text{-norbornadiene})]$ (**1**)[17] was based on literature procedures. All compounds were prepared by photochemical substitution of two CO ligands in $[W(CO)_6]$ by olefin in *n*-heptane. Complexes **2**, **3**, and **4** were purified by sublimation under vacuum at 80 °C, and complex **1** by column chromatography on silica, using *n*-heptane as the eluent. Their identity was verified by ^{1}H NMR and IR spectroscopy.

Cyclic Voltammetry. Conventional cyclic voltammograms of 10^{-3} M complexes **1**−**4** in dichloromethane containing 10^{-1} M Bu$_4$-NPF$_6$ were recorded with a PAR model 283 potentiostat, using an airtight and light-protected single-compartment cell placed in a Faraday cage. A Pt disk (0.4 mm diameter) working electrode was polished with a 0.25 μm diamond paste between scans. Coiled Pt and Ag wires served as an auxiliary and pseudoreference electrode, respectively. All electrode potentials are reported against the standard ferrocene/ferrocenium (Fc/Fc$^+$) couple. Ferrocene (BDH) or cobaltocenium hexafluorophosphate (Aldrich) were added as internal standards.[19,20] After the scans at room temperature, the cell was cooled by a dry ice−acetone slurry.

Spectroelectrochemistry. Infrared spectroelectrochemistry was carried out with a cryostatted optically transparent thin-layer electrochemical (OTTLE) cell equipped with a Pt minigrid working electrode and CaF$_2$ windows.[21] The course of the anodic electrolyses was monitored with thin-layer cyclic voltammetry and infrared spectroscopy, using a Bio-Rad FTS-7 FTIR spectrometer (16 scans, spectral resolution of 2 cm^{-1}). The OTTLE cell potential was controlled by a PA4 potentiostat (EKOM, Polná, Czech Republic). The electrolyzed dichloromethane solutions contained 5×10^{-3}

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M W(0) complex under study and 3×10^{-1} M Bu$_4$NPF$_6$ as supporting electrolyte. The thin-layer cyclic voltammograms were recorded at a scan rate of 2 mV s^{-1}.

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