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Reorientation of the Alkyne Moiety in $Fe_3(CO)_9(RC_2R)$ Clusters Induced by a Two-Electron Electrochemical Reduction

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The redox chemistry of alkyne–trimetal clusters has been investigated by electrochemical and spectroscopic techniques. The *closo*-$Fe_3(CO)_9(RC_2R)$ series undergoes two near reversible one-electron reduction steps. The bulk of spectroscopic data of the electrolytically generated $[Fe_3(CO)_9(EtC_2Et)]^{2-}$ dianion strongly suggests that the orientation of the alkyne moiety relative to the metallic triangle is changed from perpendicular to parallel. On the contrary the cathodic reduction of the nido series $FeCo_2(CO)_9(EtC_2Et)$, $Os_3(CO)_{10}(EtC_2Et)$, and $H_2M_3(CO)_9(EtC_2Et)$ (M = Ru, Os) is totally irreversible and is associated to cluster breakdown.

Introduction

The extraordinary rich chemistry of acetylene metal cluster compounds offers a variety of structural arrangements, which represent suitable models for chemisorbed hydrocarbons on metallic surface.[1] Essentially two coordination modes have been found in alkyne–trimetallic clusters. In both cases the acetylene moiety is placed above the metallic triangle: in the formally unsaturated 46-electron $Fe_3(CO)_9(RC_2R)$ series[2] the triple bond is perpendicular to a metal–metal vector, whereas the 48-electron $H_2M_3(CO)_9(RC_2R)$ (M = Ru, Os) clusters[3] have the alkyne parallel to a metal–metal bond (namely, the μ_3-η^2-$\perp$ and μ_3-η^2-$\|$ modes[1b] shown in Figure 1).

In a detailed extended Hückel molecular orbital (EHMO) study Schilling and Hoffmann[4] have explained the preference for the perpendicular orientation in the $Fe_3(CO)_9(RC_2R)$ series as a consequence of the symmetry properties of the frontier orbitals of the "$Fe_3(CO)_9$" fragment and the alkyne π orbitals; i.e., the perpendicular conformation has substantially lower energy than its parallel counterpart. A formal addition of two electrons should reverse the orientation preference, since in the parallel conformation a slightly destabilized $1a_1$ orbital is available.[4] This μ_3-η^2-$\|$ coordination mode has been experimentally found in the 48-electron $H_2M_3(CO)_9(RC_2R)$ (M = Ru, Os) clusters,[3] isoelectronic with $[Fe_3(CO)_9(RC_2R)]^{2-}$. Recent CNDO studies on $Fe_3(CO)_9(HC_2H)$[5] and $Fe_2Ru(CO)_9(HC_2H)$[6] systems are in good agreement with these features and point out the relevant role of the cluster–alkyne back-donation from the two equivalent $Fe(CO)_3$ groups.

The change in the acetylene orientation may also be accounted for by the polyhedral skeletal electron pair (PSEP) theory developed by Wade and Mingos.[7] $Fe_3(CO)_9(RC_2R)$ is a six skeletal electron pair system, $S = 6$, and therefore it should assume a closo-trigonal-bipyramidal geometry (μ_3-η^2-$\perp$); on the other hand for electron-rich complexes such as $H_2M_3(CO)_9(RC_2R)$ (M = Ru, Os), having $S = 7$, the more stable geometry is expected to be nido octahedral (μ_3-η^2-$\|$). The above change of alkyne orientation in heterometallic M_3C_2 clusters has also been forecast by EHMO calculations[8] and experimentally found as two "$Fe(CO)_3$" units (each having $S = 1.5$) are *formally* replaced in the skeletal framework by two "$Co(CO)_3$"[9] (eq 1a) or by two "$Ni(\eta^5\text{-}C_5H_5)$"[10] (eq 1b), or by each of these fragments[11] (eq 1c), both having $S = 2$.

$$\mathrm{Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}\perp\text{-}RC_2R)} \xrightarrow[-2\text{“Fe(CO)}_3\text{”}]{+2\text{“Co(CO)}_3\text{”}} \mathrm{FeCo_2(CO)_9(\mu_3\text{-}\eta^2\text{-}\|\text{-}RC_2R)} \tag{1a}$$

$$\mathrm{Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}\perp\text{-}RC_2R)} \xrightarrow[-2\text{“Fe(CO)}_3\text{”}]{+2\text{“NiCp”}} \mathrm{Fe(CO)_3Ni_2Cp_2(\mu_3\text{-}\eta^2\text{-}\|\text{-}RC_2R)} \tag{1b}$$

$$\mathrm{Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}\perp\text{-}RC_2R)} \xrightarrow[-2\text{“Fe(CO)}_3\text{”}]{+1\text{“Co(CO)}_3\text{”} + 1\text{“NiCp”}} \mathrm{FeCo(CO)_6NiCp(\mu_3\text{-}\eta^2\text{-}\|\text{-}RC_2R)} \tag{1c}$$

This paper deals with the electrochemical behavior in nonaqueous solvent of the 46-electron $Fe_3(CO)_9(RC_2R)$ series and the related electron-rich $H_2M_3(CO)_9(EtC_2Et)$ (M = Ru, Os), $Os_3(CO)_{10}(EtC_2Et)$, and $FeCo_2(CO)_9(EtC_2Et)$ systems. We wish to establish whether the electrochemical reduction can induce some change in the alkyne orientation within the organometallic skeleton.

Results and Discussion

Synthesis and Spectroscopic Data of $Fe_3(CO)_9(RC_2R)$ Series. As previously reported,[5] the best route for the title complexes, schematized in Figure 2, is the reaction of $Fe_3(CO)_{12}$ and the appropriate alkyne (1:1 molar ratio) in low boiling solvents, for relatively short reaction times (tipically 4–6 h). With use of this procedure, $Fe_3(CO)_9(EtC_2Et)$[5] (I), $Fe_3(CO)_9(PhC_2Ph)$[2] (II), $Fe_3(CO)_9(MeC_2Me)$ (III), and $Fe_3(CO)_9$(methylphenylacetylene)

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[1] (a) Ugo, R. *Catal. Rev.* **1975**, *11*, 225. (b) Muetterties, E. L.; Rhodin, T. N.; Band, E.; Brucker, C. F.; Pretzer, W. R. *Chem. Rev.* **1979**, *79*, 91.

[2] Blount, J. F.; Dahl, L. F.; Hoogzand, C.; Hübel, W. *J. Am. Chem. Soc.* **1966**, *88*, 292.

[3] (a) Mason, R.; Thomas, K. M. *Ann. N.Y. Acad. Sci.* **1974**, *239*, 225. (b) Goudsmit, R. J.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Rosales, M. J. *J. Chem. Soc., Dalton Trans.* **1983**, 2257.

[4] Schilling, B. E. R.; Hoffmann, R. *J. Am. Chem. Soc.* **1979**, *101*, 3456.

[5] Granozzi, G.; Tondello, E.; Casarin, M.; Aime, S.; Osella, D. *Organometallics* **1983**, *2*, 430.

[6] Busetti, V.; Granozzi, G.; Aime, S.; Gobetto, R.; Osella, D. *Organometallics* **1984**, *3*, 1510.

[7] For a very recent discussion see: Mingos, D. M. P. *Acc. Chem. Res.* **1984**, *17*, 311 and references therein.

[8] Halet, J.-F.; Saillard, J.-Y.; Lissillour, R.; McGlinchey, M. J.; Jaouen, G. *Inorg. Chem.* **1985**, *24*, 218.

[9] Aime, S.; Milone, L.; Osella, D.; Tiripicchio, A.; Manotti-Lanfredi, A. M. *Inorg. Chem.* **1982**, *21*, 501.

[10] Sappa, E.; Manotti-Lanfredi, A. M.; Tiripicchio, A. *J. Organomet. Chem.* **1981**, *221*, 93.

[11] Jaouen, G.; Marinetti, A.; Mentzen, B.; Mutin, R.; Saillard, J.-Y.; Sayer, B. G.; McGlinchey, M. J. *Organometallics* **1982**, *1*, 753.

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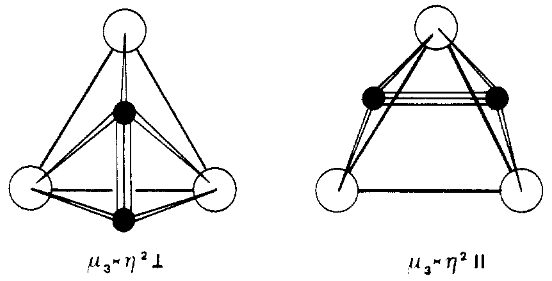

Figure 1. Sketch of the two basic bonding modes between the alkyne and a metallic triangle.

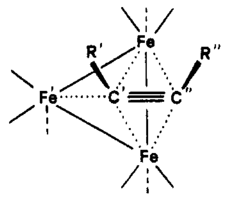

Figure 2. Schematic structures of the $Fe_3(CO)_9(\mu_3$-η^2-$\perp$-alkyne) series: R' = R'' = Et, I; R' = R'' = Ph, II; R' = R'' = Me, III; R' = Me, R'' = Ph, IVA; R' = Ph, R'' = Me, IVB.

(two isomers) were synthesized in reasonably good yields (Table I).

Several alkynes bearing substituent groups with pronounced electron-withdrawing or electron-releasing properties, as $C_2(COOMe)_2$, $C_2(CH_2OH)_2$, and $C_2(CH_2NMe_2)$, were employed in the above-mentioned experimental conditions, but no products of formula $Fe_3(CO)_9(RC_2R)$ could be achieved: the main products being always the "ferrole" derivatives $Fe_2(CO)_6(alkyne)_2$, along with the butatriene complex $Fe_2(CO)_6(MeC{=}C{=}C{=}CH_2)$ for the diol ligand only.[12] Thus the μ_3-η^2-$\perp$ bonding mode seems to be thermodynamically stable only for unfunzionalized aliphatic or aromatic substituents, which do not strongly perturb the delicate alkyne–cluster charge balance.[5,6] In Table I the ^1H and ^{13}C NMR data of the $Fe_3(CO)_9(RC_2R)$ series are summarized. The proposed assignment is similar to that of $Fe_3(CO)_9(EtC_2Et)$ previously discussed.[5] The resonances assigned to C' atoms and their R' substituents show a marked downfield shift probably due to the paramagnetic deshielding effect of the non-bonding electrons of all the three iron atoms. From the reaction of methylphenylacetylene a product, apparently pure, is obtained from TLC separation and subsequent *n*-heptane crystallization. However ^1H and ^{13}C NMR spectra unambiguously reveal that it is an inseparable mixture of two isomers, i.e., $Fe_3(CO)_9(MeC_2Ph)$ (IVA) and $Fe_3(CO)_9(PhC_2Me)$ (IVB). The ^1H NMR spectrum shows two singlets at δ 3.05 and 1.10 in an integrated intensity ratio of ~2:1, along with a nondiagnostic broad multiplet in the aromatic region. The downfield methyl resonance is associated to structure IVA, which represents the twice abundant isomer. This feature is consistent with CNDO results of the $Fe_3(CO)_9(HC_2H)$ model complex,[5] in which the C' atom results to be positively charged; thus the thermodynamically more stable isomer should have the electron-releasing CH_3 group on C' (IVA) instead of the Ph group (IVB).

Further support to the occurrence of this isomerism comes from the ^{13}C NMR of a ^{13}CO-enriched (~20%) sample of IVA and IVB mixture. At room temperature both resonances typical of the $Fe_3(CO)_9(RC_2R)$ series (assigned to the two equivalent $Fe(CO)_3$ sets and to the $Fe'(CO)_3$ unit, respectively, in rapid localized exchange)

Table I. Spectroscopic Data of $Fe_3(CO)_9(\mu_3$-η^2-$\perp$-Alkyne) Series

				^1H NMR[b,c] δ		^{13}C NMR[b,c] δ					
compd	no.	yield, %	IR[a] ν_{CO}, cm^{-1}	R'	R''	C'	C''	$Fe(CO)_3$	$Fe'(CO)_3$	R'	R''
$Fe_3(CO)_9(EtC_2Et)$	I	25	2078 m, 2031 vs, 2023 vs, 2006 s, 1994 w, 1991 w	3.60 (q, 2), 1.72 (t, 3)	1.63 (q, 2), 0.48 (t, 3)	221.9	106.8	212.2	207.9	39.5 (CH_2), 16.5 (CH_3)	21.8 (CH_2), 15.4 (CH_3)
$Fe_3(CO)_9(PhC_2Ph)$	II	20	2081 m, 2041 vs, 2027 vs, 2012 s, 1995 w, 1985 w	7.35 + 5.88 (m, 10)		214.1	107.0	211.5	206.4	147.5–123.3	
$Fe_3(CO)_9(MeC_2Me)$	III	10	2080 m, 2033 vs, 2025 vs, 2008 s, 1997 w, 1992 w	3.36 (s, 3)	1.18 (s, 3)	214.9	99.3	211.4	207.7	32.7	16.5
$Fe_3(CO)_9(MeC_2Ph)$	IVA	15[d]	2081 m, 2035 vs, 2025 vs, 2010 s, 1999 w, 1984 w	3.05 (s, 3)	7.65 + 5.90 (m, 5)	215.7	104.3	211.4	207.1	32.6	148.5–125.4
$Fe_3(CO)_9(PhC_2Me)$	IVB			7.65 + 5.90 (m, 5)	1.10 (s, 3)	214.0	104.2	211.5	207.2	148.5–125.4	18.1

[a] *n*-Hexane. [b] $CDCl_3$ at +25 °C. [c] Assignment according to Figure 2. [d] TLC and column inseparable mixture of two isomers.

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[12] Victor, R. *J. Organomet. Chem.* 1977, *127*, C25.

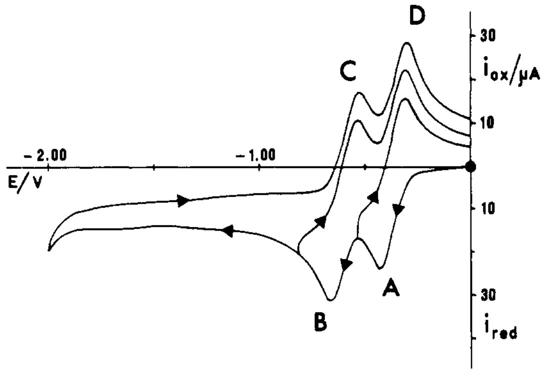

Figure 3. Cyclic voltammogram recorded on a CH_2Cl_2 solution containing II (1.1×10^{-3} mol dm^{-3}) and $[NBu_4][ClO_4]$ (0.1 mol dm^{-3}) [mercury working electrode; scan rate 0.2 V s^{-1}; (●) starting potential].

are split in two very close signals ($\Delta\delta = 0.1$ ppm) in an integrated intensity ratio of ~1:2 [211.5, 211.4, 207.2, and 207.1 ppm, respectively].

Dynamics of the $Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}\perp\text{-Alkyne})$ Complexes. The occurrence of the two isomers, namely, $Fe_3(CO)_9(MeC_2Ph)$ (IVA) and $Fe_3(CO)_9(PhC_2Me)$ (IVB), enables us to check the alkyne rotation within the μ_3-η^2-⊥-alkyne clusters by variable-temperature NMR spectroscopy. Deeming has clearly demonstrated that such rotation occcurs in the related $H_2M_3(CO)_9(\mu_3\text{-}\eta^2\text{-}\|\text{-alkyne})$ (M = Ru, Os) complexes;[13] furthermore Schilling and Hoffmann have calculated the possible transition states for the acetylene rotation in $Fe_3(CO)_9(HC_2H)$.[14] Since the ^1H NMR resonances of the methyl group in the two isomers have quite different chemical shifts ($\Delta\delta = 1.95$ ppm) and the ^{13}C NMR resonances of the $Fe(CO)_3$ units in the two isomers have very close chemical shifts ($\Delta\delta = 0.1$ ppm), we have recorded variable temperature ^1H NMR spectra at low field (JEOL 60) and variable-temperature ^{13}C NMR spectra at high field (JEOL 270) in order to fit a suitable range of temperatures. Obviously in both cases if the alkyne rotation occurs, it should interconvert the two isomers and hence render equivalent the methyl as well as the $Fe(CO)_3$ resonances. This coalescence has not been observed up to +100 °C, where the sample begins to show incipient decomposition. These experiments would lead to $\Delta G^* > 74.8$ and >85.9 KJ/mol in the ^1H and ^{13}C frequency scales, respectively.[15] Thus, even if the rotation of the alkyne moiety would occur in μ_3-η^2-⊥-alkyne clusters, its energy barrier is much higher than that of the parallel homologues.[13] This different behavior has to be considered as regiospecific reactions of these complexes are concerned. The different dynamics are not surprising from the PSEP viewpoint: the $H_2M_3(CO)_9(RC_2R)$ (M = Ru, Os) series is classifiable as nido octahedron and the $Fe_3(CO)_9(RC_2R)$ series as closo trigonal bipyramid; thus only the former has a vacancy on the cluster surface that may be associated to high fluxionality.[16]

Electrochemical Behavior of the $Fe_3(CO)_9(RC_2R)$ Series. The cyclic voltammetric response of a CH_2Cl_2 solution of $Fe_3(CO)_9(PhC_2Ph)$ (II) at a mercury electrode is reported in Figure 3. As it can be seen, two distinct subsequent cathodic processes are present. Controlled potential coulometric tests at −1.0 V show that the two processes globally consume 2 mol of electrons/mol of starting compound, so indicating each reduction step to involve a one-electron charge transfer.

An analysis of the cyclic voltammetric responses with scan rate has been performed.[17] In the scan rate range from 0.02 to 10 V s^{-1} (at higher scan rates the response becomes ill-defined) the cathodic process occurring at peak A showed the following features: the anodic to cathodic peak current ratio $i_{p(D)}/i_{p(A)}$ is constantly equal to unity; the ratio between the cathodic peak current and the square root of the scan rate $i_{p(A)}/v^{1/2}$ is substantially constant; the difference between the peak potential value of the cathodic peak A and that of its directly associated reoxidation peak D, ΔE_p, gradually increases from 77 to 360 mV. All these findings, which are typical for an uncomplicated one-electron quasi-reversible charge transfer, indicate that in the first redox process the neutral cluster is reversibly reduced to the corresponding monoanion (0/1−). The same features are found for the more cathodic process occurring in the correspondence of peak B and its directly associated peak C; the only difference is a slightly minor degree of reversibility, since in the above-cited scan rate range the ΔE_p value increases from 86 to 480 mV. Therefore it can be deduced that in the more cathodic process the electrogenerated monoanion cluster is reversibly reduced to the corresponding dianion (1−/2−).

These results allow a reliable evaluation of the formal electrode potential $E°'$ of each reduction step as the mean value between the peak potential value of the cathodic response and that of its directly associated anodic response, in the likely hypothesis that the transfer coefficient α ranges between 0.3 and 0.7.

The same results are obtained by using a platinum working electrode. In this case it is possible to reveal also the occurrence of an oxidation process showing an anodic peak, not well reproducible, with a directly associated cathodic one in the reverse scan. The peak height of the anodic response is indicative of a multielectron process, as well as the cathodic to anodic peak current ratio, notably lower than unity, is indicative of a charge transfer complicated by following chemical reactions. The closeness of the response to the solvent discharge and its low reproducibility discouraged us from a deep investigation on the underlying electrode mechanism by coulometry and chronoamperometry; however, it seems not ventured to hypothesize, also by comparison with alkyne–triruthenium clusters,[18] the occurrence of an electrode mechanism of the ECE type, or an even more complicated type (ECEC...); this means that the loss of electrons very likely leads to destruction of the cluster framework.

In addition the use of platinum electrodes allows us a rough computation of the heterogeneous rate constant, k_s, for the 0/1− charge transfer, through Nicholson's treatment,[19] evaluating the diffusion coefficient of the cluster by comparison with the response from ferrocene. In this connection a diffusion coefficient value of $D_0 = D_R = 1.6 \times 10^{-5}$ cm^2 s^{-1} has been attributed to ferrocene in CH_2Cl_2 on the basis of Walden's rule applied to different solvents.[20] This k_s value is equal to 3.4×10^{-3} cm s^{-1}, which confirms the quasi-reversibility of the charge transfer.

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[13] (a) Deeming, A. J. *J. Organomet. Chem.* **1978**, *150*, 123. (b) Evans, J.; McNulty, G. S. *J. Chem. Soc., Dalton Trans.* **1981**, 2017.

[14] Schilling, B. E. R.; Hoffmann, R. *Acta Chem. Scand., Ser. B* **1979**, *B33*, 231.

[15] Activation energies are obtained by using the approximate equation: $\Delta G^* = 4.576T_c\,[9.97 + \log T_c/\Delta\nu]$; see: Kost, D.; Carlson, E. H.; Raban, M. *J. Chem. Soc., Chem. Commun.* **1971**, 656.

[16] McGlinchey, M. J.; Mlekuz, M.; Bougeard, P.; Sayer, B. G.; Marinetti, A.; Saillard, J. Y.; Jaouen, G. *Can. J. Chem.* **1983**, *61*, 1319.

[17] Brown, E. R.; Large, R. F. In *Techniques of Chemistry*; Weissberger, A., Rossiter, B. W., Eds.; Wiley-Interscience: New York, 1971; Vol. I, Part IIA, Chapter VI.

[18] Zanello, P.; Aime, S.; Osella, D. *Organometallics* **1984**, *3*, 1374.

[19] Nicholson, R. S. *Anal. Chem.* **1965**, *37*, 1351.

[20] Konopka, S. J. Jun., University Microfilms International, Ann Arbor, MI, No. 7124622.

Table II. Redox Potentials (in V, vs. SCE) for the Electron-Transfer Processes in Which Cluster Compounds I–VIII Undergo in CH_2Cl_2 Solution Containing $[NBu_4][ClO_4]$ (0.1 mol dm^{-3}) Supporting Electrolyte[a]

	reduction steps		oxidation step	
cluster	$E°'(0/1-)$	$E°'(1-/2-)$	$(E_p)_a$	$(E_p)_c$
(I) $Fe_3(CO)_9(EtC_2Et)$	−0.49	−0.67	+1.42	+1.05
(II) $Fe_3(CO)_9(PhC_2Ph)$	−0.36	−0.60	+1.35	+1.05
(III) $Fe_3(CO)_9(MeC_2Me)$	−0.47	−0.65	+1.29	+1.08
(IV) $Fe_3(CO)_9(C_2Ph, Me)$[d]	−0.43	−0.62	+1.33	...
(V) $FeCo_2(CO)_9(EtC_2Et)$	−0.86	−1.09	...	...
(VI) $Os_3(CO)_{10}(EtC_2Et)$	−1.46[b]	...	+1.33	...
(VII) $H_2Ru_3(CO)_9(EtC_2Et)$	−1.74[c]		+1.18	...
(VIII) $H_2Os_3(CO)_9(EtC_2Et)$	−2.02[c]		+1.35	...

[a] Peak potential values refer to 0.2 V s^{-1}. [b] Peak potential value. [c] Peak potential value for the two-electron charge transfer (0/2−). [d] Mixture of two isomers (IVa and IVb, see text) undistinguishable in electrochemical experiments.

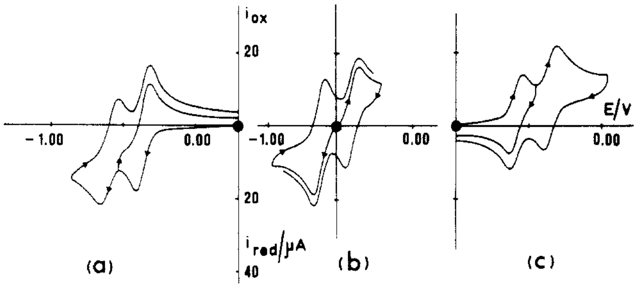

Figure 4. Cyclic voltammetric responses at a platinum electrode from a CH_2Cl_2 solution containing II (1.15×10^{-3} mol dm^{-3}) and $[NBu_4][ClO_4]$ (0.1 mol dm^{-3}) in the following conditions: initial (a); after the consumption of one electron per molecule of II by controlled potential electrolysis at a platinum macroelectrode at −0.5 V (b); after the consumption of one further electron per molecule of II by electrolysis at −1.0 V (c) [scan rate 0.2 V s^{-1}; (●) starting potential].

The above-cited electrochemical scenario is typical for all the closo-trigonal-bipyramidal clusters I–IV, and their most significant redox characteristics are summarized in Table II.

It is noteworthy that cyclic voltammetry suggests that for these compounds both the electrogenerated monoanion and dianion are fairly stable products, as clearly shown in Figure 4, in which the step-by-step electrolytic reduction of II is followed.

It is remarkable that the two subsequent charge transfers are not followed by the chemical complications typical for both the parent compound $Fe_3(CO)_{12}$[21,22] and its phosphine-[22] or sulfur-substituted[23] derivatives. This enhanced stability is certainly due to the flexibility of the acetylene coordination mode.

Since it is very difficult to separate the electrogenerated $[Fe_3(CO)_9(RC_2R)]^{2-}$ dianion from the very large excess of TBAP, or TEAP, supporting electrolyte employed in CH_2Cl_2 solution and this does not allow us to record suitable NMR spectra, we have tested some nonaqueous solvents in which alkali-metal perchlorates are soluble. While MeCN causes complete solvolytic decomposition of these clusters, acetone is shown to be a suitable solvent. In it the mechanisms involved in the cathodic reduction of I–IV derivatives substantially parallel those previously described in CH_2Cl_2; there is only a higher difference between the reduction potentials for the first and the second electron-transfer steps. In addition some electrode poisoning phenomena have been noted. The slightly different behavior in the two solvents has been also observed for other trinuclear carbonyl cluster compounds.[22] Table III summarizes the redox potentials obtained for the compounds under study in acetone/$NaClO_4$ solution.

Table III. Redox Potentials (in V, vs. SCE) of Compounds I–VIII in Me_2CO Solution Containing $NaClO_4$ (0.1 mol dm^{-3}) Supporting Electrolyte[a]

cluster	$E°'(0/1-)$	$E°'(1-/2-)$
I	−0.39	−0.76
II	−0.33	−0.65
III	−0.40	−0.75
IV	−0.33	−0.70
V	−0.70	−1.12
VI	−1.17[b]	
VII	−1.60[c]	
VIII	...	

[a] Peak potential values refer to 0.2 V s^{-1}. [b] Peak potential value. [c] Peak potential value for the two-electron charge transfer (0/2−).

Solution Structure of $[Fe_3(CO)_9(EtC_2Et)]^{2-}$. The $Fe_3(CO)_9(EtC_2Et)$ parent cluster has been chosen for exhaustive macroelectrolyses since its ethyl resonances should result in quite diagnostic NMR experiments. A number of exhaustive (two electrons) electrolyses were carried out by using CH_2Cl_2 as solvent (TBAP or TEAP as supporting electrolyte) or alternatively acetone as solvent ($LiClO_4$ or $NaClO_4$ as supporting electrolyte). The close similarity of the IR pattern (apart from some frequency shift probably due to ion-pairing phenomena[24]) of the electrolyzed solutions confirms that the electrogenerated product is the same in all the experimental conditions employed (Table IV). Attempts to crystallize the red dianion were unsuccessful. From all the electroreduced solutions, the parent cluster $Fe_3(CO)_9(EtC_2Et)$ can be easily recovered by oxidation with solid $AgBF_4$ or $AgPF_6$ and subsequent SiO_2 column purification (up to 60% yield). This indicates that no drastic declusterification has occurred, and it suggests an overall stoichiometry:

$$\begin{tikzcd}
Fe_3(CO)_9(EtC_2Et) \arrow[r, shift left, "+1e^-"] & {[Fe_3(CO)_9(EtC_2Et)]^{-\cdot}} \arrow[l, shift left] \arrow[d, shift left, "+1e^-"] \\
& {[Fe_3(CO)_9(EtC_2Et)]^{2-}} \arrow[u, shift left] \arrow[lu, "+2Ag^+"]
\end{tikzcd}$$

Interestingly the reactivity of $[Fe_3(CO)_9(EtC_2Et)]^{2-}$ depends upon the nature of the counterion, being much higher for Li^+ or Na^+ than for $[Bu_4N]^+$ or $[Et_4N]^+$ cations.[25] However the dianion, even if associated to alkali-metal cations, is stable in the solid state for some days, provided that oxygen and water are *rigorously* excluded.

In NMR experiments acetone was removed from the electrolyzed solution under dry nitrogen flux and the

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(21) Miholovâ, D.; Fiedler, J.; Vlcek, A. A. *J. Electroanal. Chem.* **1983**, *143*, 195 and references therein.

(22) Bond, A. M.; Dawson, P. A.; Peake, M. B.; Robinson, B. H.; Simpson, J. *Inorg. Chem.* **1977**, *16*, 2199.

(23) Madach, T.; Vahrenkamp, H. *Chem. Ber.* **1981**, *114*, 505.

(24) Chen, C. K.; Cheng, C. H. *Inorg. Chem.* **1983**, *22*, 3378.

(25) Kirk, C. M.; Peake, B. M.; Robinson, B. H.; Simpson, J. *Aust. J. Chem.* **1983**, *36*, 441.

Table IV. Spectroscopic Data of the $[Fe_3(CO)_9(EtC_2Et)]^{2-}$ Dianion

counterion	IR ν_{CO}/cm^{-1}	^1H NMR[c] δ		^{13}C NMR[c] (organic region) δ	
$[NBu_4]^+$	2027 m, 1971 vs, 1932 s, 1918 w[a]				
$[NEt_4]^+$	2028 m, 1973 vs, 1931 s, 1920 w[a]				
$[Li]^+$	2024 m, 1998 vs, 1972 s, 1901 w[b]	3.21 (q, 4)	1.31 (t, 6)	39.3 (CH_2)	[d] 18.4 (CH_3)
$[Na]^+$	2024 m, 1998 vs, 1968 s, 1957 w[b]	3.19 (q, 4)	1.34 (t, 6)	39.5 (CH_2)	[d] 18.5 (CH_3)

[a] CH_2Cl_2. [b] Me_2CO. [c] CD_2Cl_2, at +25 °C, after filtration of the excess of alkali-metal perchlorate (see text). [d] A weak signal at *ca.* 169 ppm is observed for both alkali salts; it is assigned to two equivalent acetylenic carbon atoms.

white-red residue extracted with CD_2Cl_2 and subsequently filtered in glovebox. This procedure allowed us to eliminate $LiClO_4$, almost insoluble in dichloromethane, while the dianion is fairly soluble in such solvent. The proton NMR spectrum of this solution unambiguously indicates that $[Fe_3(CO)_9(EtC_2Et)]^{2-}$ is a *diamagnetic* substance, since no shift and broadening is observed for the absorption of the internal reference Me_4Si.[26] Thus both electrons are added to the same molecular orbital giving rise to a singlet spin state. While for the parent compound $Fe_3(CO)_9(EtC_2Et)$ both ^1H and ^{13}C NMR spectra show a large spread of chemical shifts of the ethyl groups, in $[Fe_3(CO)_9(EtC_2Et)]^{2-}$ the two substituents are equivalent at room temperature, being shifted downfield in respect to the average values of the parent cluster (Table IV), as expected for a doubly charged species.[27] Furthermore the ^{13}C NMR spectrum of the dianion exhibits a single weak signal at ca. 169 ppm in the acetylenic carbon region. The more straightforward explanation for this equivalence is that the alkyne is now parallel to an iron–iron vector, and it is engaged in a rapid rotation over the metallic triangle.[13]

The variable temperature ^{13}C NMR spectrum of a ^{13}CO-enriched (~20%) sample of $[Fe_3(CO)_9(EtC_2Et)]^{2-}$ is reported in Figure 5. The low-temperature limiting spectrum (−92 °C) shows four resonances at 218.4, 214.5, 214.3, and 213.6 ppm in integrated intensities of 3:2:2:2. This spectrum is consistent (even if it does not *unambiguously* prove this) with the proposed μ_3-η^2-|| coordination mode in the dianion. The downfield resonance is assigned to the π-bound $Fe(CO)_3$ unit, whose localized exchange is not completely frozen on NMR time scale; the two very close resonances at 214.5 and 214.3 ppm and that at 213.6 ppm are attributed to the two very similar equatorial and axial sets of COs of the two σ-bound $Fe(CO)_3$ moieties, respectively. As the temperature is increased, localized exchange at the two equivalent $Fe(CO)_3$ units causes the progressive coalescence of the three resonances of intensity 2, and finally at room temperature the total scrambling of all the COs (single broad peak at 215.7 ppm) is likely due to the rapid rotation of the alkyne over the metallic triangle, as found in the neutral μ_3-η^2-||-alkyne clusters.[18]

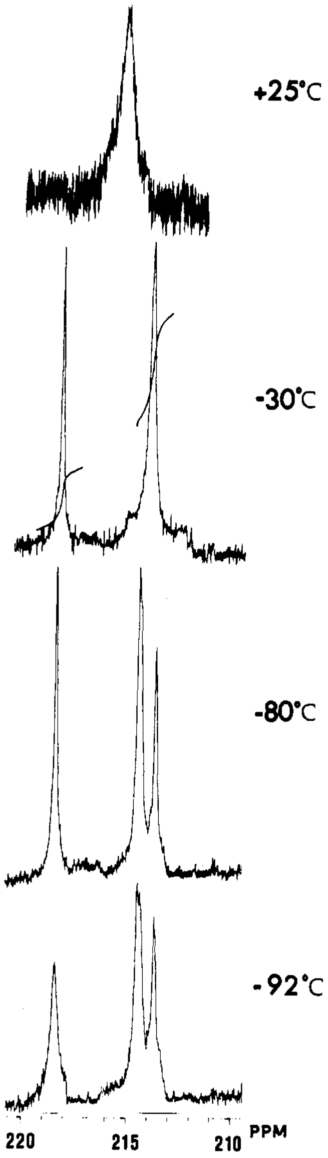

Figure 5. Variable-temperature ^{13}C NMR of $[Li]_2[Fe_3(CO)_9(EtC_2Et)]$ in the carbonyl region in CD_2Cl_2.

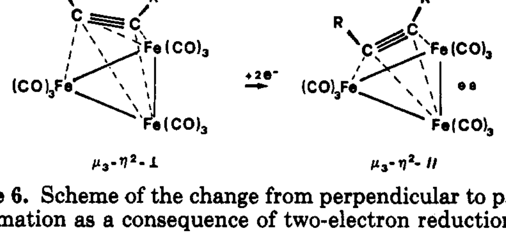

Figure 6. Scheme of the change from perpendicular to parallel conformation as a consequence of two-electron reduction.

In conclusion, the bulk of electrochemical and spectroscopic data strongly suggests that, as expected from theoretical calculations,[4,8] the alkyne assumes a configuration parallel to a iron–iron vector as a consequence of the two-electron reduction (Figure 6). Since this conformational change is so quick that it cannot be revealed even by the fast voltammetric techniques used here, it must be deduced that it occurs *concomitant with*, rather than *subsequent to*, the charge transfers. Structural isomerizations concomitant with electron transfers are uncommon and only recently have been focused.[28] In electrochemical terms the unique feature seems to be a retardation of the rate of the relevant charge transfers; in thermodynamic terms it seems likely that the closeness of the two reduction steps may be assumed as a further diagnostic parameter for the favored closo to nido reorganization. The fact that, independently from the electrode material and from the solvent, both the charge transfers are quasi-reversible

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(26) Evans, D. F. *J. Chem. Soc., Dalton Trans.* **1959**, 2003.

(27) Aime, S.; Milone, L. *Prog. Nucl. Magn. Reson. Spectrosc.* **1977**, *11*, 183.

(28) (a) Bowyer, W. J.; Geiger, W. E. *J. Am. Chem. Soc.* **1985**, *107*, 5657. (b) Tulyathan, B.; Geiger, W. E. *J. Am. Chem. Soc.* **1985**, *107*, 5960.

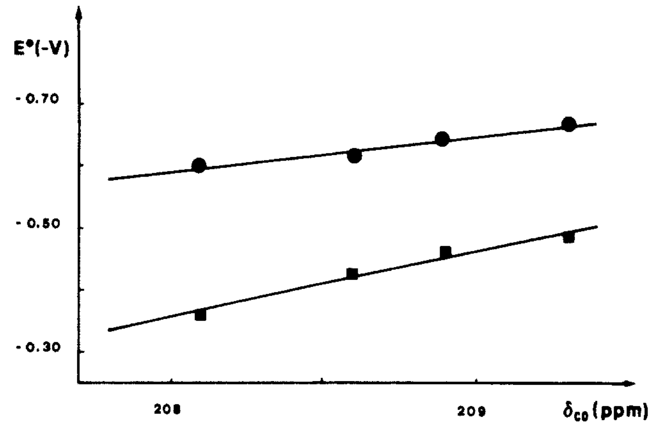

Figure 7. Plot of $E^{\circ\prime}$ in CH_2Cl_2 for the two reduction steps [0/1− (■); 1−/2− (●)] against $\delta(^{13}C)$ weighted average of CO groups of $Fe_3(CO)_9(RC_2R)$ derivatives. The least-squares slopes are −0.11 V/ppm (■) and −0.06 V/ppm (●), and the correlation coefficients are 0.98 (■) and 0.97 (●), respectively.

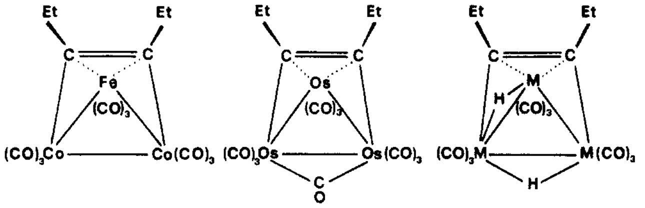

Figure 8. Schematic structure of the nido complexes, namely, $FeCo_2(CO)_9(EtC_2Et)$ (V), $Os_3(CO)_9(\mu\text{-}CO)(EtC_2Et)$ (VI), and $H_2M_3(CO)_9(EtC_2Et)$ [M = Ru (VII); M = Os (VIII)].

should be consequently interpreted, thinking the alkyne reorientation to be fully completed only after the two-electron reduction, even if it has been foreseen[8] that 6.5 skeletal electron pair systems tend to assume a nido geometry.

Relationship between Electrode Potentials and NMR Parameters of $Fe_3(CO)_9(RC_2R)$ Series. The correlation between NMR chemical shifts and electrochemical data has already been discussed by Bond et al.[29] and verified by us for some organotriruthenium clusters.[18] When both these parameters are essentially governed by electronic effects and deep geometrical changes are avoided, a linear correlation (via free energy) is expected. In Figure 7 the formal electrode potentials $E^{\circ\prime}$ of each reduction step of the $Fe_3(CO)_9(RC_2R)$ series are plotted against the weighted average $\delta(^{13}CO)$ values. A linear correlation holds for both reduction sets, but, due to the close similarity of the electronic effect of the alkyne substituents, the level of significance is lower than that in previous studies.[18,29]

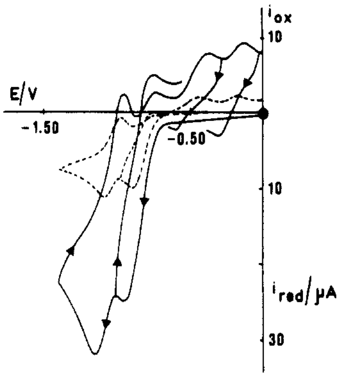

Figure 9. Cyclic voltammograms from a CH_2Cl_2 solution of V (1.3×10^{-3} mol dm^{-3}) containing $[NBu_4][ClO_4]$ (0.1 mol dm^{-3}): (—) 0.5 V s^{-1}; (- - -) 0.05 V s^{-1} [platinum working electrode; (●) starting potential].

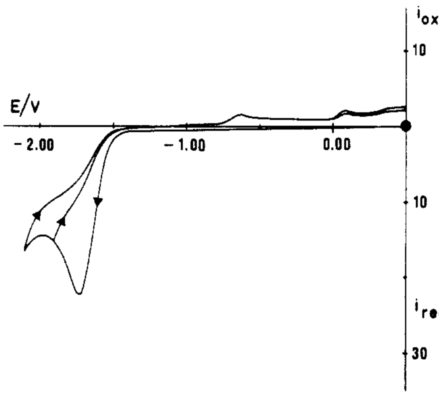

Figure 10. Cyclic voltammetric response recorded on a CH_2Cl_2 solution of VII (9.6×10^{-4} mol dm^{-3}) containing $[NBu_4][ClO_4]$ (0.1 mol dm^{-3}) [platinum working electrode; scan rate 0.2 V s^{-1}; (●) starting potential].

Electrochemical Behavior of the 48-Electron Alkyne–Trimetallic Clusters. On passing to the electron-rich nido homologues, namely, $FeCo_2(CO)_9(EtC_2Et)$[9] (V), $Os_3(CO)_9(\mu\text{-}CO)(EtC_2Et)$[30] (VI), and $H_2M_3(CO)_9(EtC_2Et)$ [M = Ru (VII); M = Os (VIII)][31] (Figure 8), the reduction process is expected to be much less facile than that associated to the "unsaturated" $Fe_3(CO)_9(RC_2R)$ series. This is indeed the case; the difficulty of the charge transfers practically increases from V to VIII according to the effect induced by heavier metals.[22] The electrochemical behavior is substantially the same at both the platinum and mercury electrodes, as well as in CH_2Cl_2 and Me_2CO solvents (see Tables II and III).

Figure 9 reports the cyclic voltammetric curves recorded in CH_2Cl_2 solution of V at two different scan rates.

It can be easily noted that also in this case both the monoanion and the dianion are electrogenerated, but the monoanion is a quite labile product. In fact only increasing the scan rate allows to put in evidence of an anodic peak directly associated to the 0/1− charge transfer. In the scan rate range from 0.2 to 2 V s^{-1} the anodic to cathodic peak current ratio assumes the values from 0.58 to 0.84. On the other hand the decomposition of electrogenerated anions is well documented also by the appearance of the two peak systems at $E^{\circ\prime}$ = −0.23 and −0.51 V, respectively, in the reverse scan, attributable to the reoxidation of declusterification products. A rough evaluation of the lifetime of the monoanion leads to a $t_{1/2}$ value of about 0.3 s.[32] It has to be noted that, on the basis of the cyclic voltammetric responses, the dianion seems to be kinetically more stable than the monoanion. It must be noted that this unusual behavior has been previously reported for the $RCCo_2M(CO)_8Cp$ [R = Me, Ph; M = Cr, Mo, W].[33]

The cathodic behavior of VI appears as a reduction peak (E_p = −1.46 V at 0.2 V s^{-1}), to which no directly associated reoxidation peak could be evidenced even at 100 V s^{-1}. The comparison with the response of ferrocene indicates that this cathodic peak is due to a one-electron process. By analogy with other trinuclear–alkyne clusters,[18] it can be thought that the lack of a directly associated anodic peak

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(29) Bond, A. M.; Carr, S. W.; Colton, R.; Kelly, D. P. *Inorg. Chem.* **1983**, *22*, 989.

(30) Deeming, A. J.; Hasso, S.; Underhill, M. J. *J. Chem. Soc., Dalton Trans.* **1975**, 1614.

(31) Domingos, A. J. P.; Johnson, B. F. G.; Lewis, J. *J. Organomet. Chem.* **1972**, *36*, C43.

(32) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706.

(33) Lindsay, P. N.; Peake, B. M.; Robinson, B. H.; Honrath, U.; Vahrenkamp, H.; Bond, A. M. *Organometallics* **1984**, *3*, 413.

has to be attributed to the quickness of the monoanion destruction rather than to the irreversibility of the heterogeneous charge transfer; in addition it seems likely that the electrode formation of the dianion takes place at potentials more negative than the solvent discharge itself. Also in this case a reoxidation peak, indicative of the decomposition of the cluster anion, is present in the reverse scan at about −0.3 V, well anodic to the cathodic peak.

Finally compounds VII and VIII reduce through similar cathodic processes involving one two-electron step. In both cases the relevant cathodic peak shows the typical features due to a charge transfer totally irreversible in character. As an example Figure 10 shows the response from VII.

Thus the electrochemical reduction process of μ_3-η^2-$\|$-alkyne clusters results to be completely irreversible, giving rise to a rapid declusterification. This is consistent with the EHMO picture of Schilling and Hoffman:[4] for a 48-electron species just a highly destabilized asymmetric MO (having metal–metal antibonding character due to its parentage with the $2e_a$ orbital) is available, so the added electrons cause strong destabilization of the entire polyhedral frame.

Experimental Section

The $Fe_3(CO)_9(RC_2R)$ (I–IV) clusters were synthesized from $Fe_3(CO)_{12}$ and the appropriate alkyne in 1:1 molecular ratio in *n*-hexane at reflux under N_2 for 4 h (MeC_2Me and EtC_2Et) or 6 h (PhC_2Me and PhC_2Ph). The separations of the reaction mixture were carried out on TLC plates (SiO_2, eluant petroleum ether–diethyl ether, 9:1 v/v). The preparation of ^{13}CO-enriched samples of $Fe_3(CO)_9(RC_2R)$ complexes was performed by a similar procedure using $Fe_3(CO)_{12}$, ~20% enriched in ^{13}CO, as the starting material.

Compounds V–VIII were synthesized according to the published procedures.[9,30,31] After crystallization in *n*-heptane at 0 °C, purity of all tested complexes was checked by IR and ^1H and ^{13}C NMR spectroscopy.

The IR spectra were recorded on a Perkin-Elmer 580 B instrument and the ^1H and ^{13}C NMR on a JEOL GX-270-89 machine (for variable-temperature ^1H NMR experiments a JEOL C-60-HL was also employed).

The electrochemical apparatus has been described elsewhere.[34] Potential values refer to a saturated aqueous calomel electrode (SCE). The temperature was controlled at 20 ± 0.1 °C. The exhaustive macroelectrolysis of $Fe_3(CO)_9(EtC_2Et)$ (I) was brought about at the controlled potential of −1.0 V by using a platinum gauze working macroelectrode. As the two-electron reduction proceeds, the solution turns from brown into dark-red. All the manipulations of the electrogenerated $[Fe_3(CO)_9(EtC_2Et)]^{2-}$ dianion were carried out in a glovebox purged with dry dinitrogen. The solvents used for electrochemistry, dichloromethane and acetone, were from Burdick and Jackson, were "distilled in glass", and were used without purification. Tetrabutylammonium perchlorate (TBAP, Fluka) and tetraethylammonium perchlorate (TEAP, Carlo Erba) supporting electrolytes were dried in a vacuum oven and used without further purification. Lithium perchlorate and sodium perchlorate supporting electrolytes were prepared by neutralizing perchloric acid with the corresponding alkali carbonate, twice crystallizing from methanol, and finally drying at 110 °C. Bis(η^5-cyclopentadienyl)iron(II) (ferrocene, Alfa Products) was used as purchased. Extra pure dinitrogen was employed to remove oxygen from tested solutions.

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Registry No. I, 69402-19-3; II, 12171-93-6; III, 101315-98-4; IVa, 101315-99-5; IVb, 101316-00-1; V, 78109-40-7; VI, 101316-01-2; VII, 80303-37-3; VIII, 101316-02-3; $[Fe_3(CO)_9(EtC_2Et)][NBu_4]_2$, 101316-04-5; $[Fe_3(CO)_9(EtC_2Et)][NEt_4]_2$, 101316-05-6; $[Fe_3(CO)_9(EtC_2Et)]Li_2$, 101400-35-5; $[Fe_3(CO)_9(EtC_2Et)]Na_2$, 101316-06-7; Fe, 7439-89-6; Os, 7440-04-2.

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[34] Zanello, P.; Seeber, R.; Cinquantini, A.; Mazzocchin, G. A.; Fabbrizzi, L. *J. Chem. Soc., Dalton Trans.* **1982**, 893.

Methyl–Ethylene and Methyl–Carbonyl Complexes of Platinum(II) and Platinum(IV)

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The methyl(ethylene)platinum(II) complex $[Pt_2(\mu\text{-}Cl)_2Me_2(C_2H_4)_2]$ and methylcarbonylplatinum(II) complex $[Pt_2(\mu\text{-}Cl)_2Me_2(CO)_2]$ have been prepared and characterized. Reactions of $[Pt_2(\mu\text{-}Cl)_2Me_2(C_2H_4)_2]$ with alkenes or alkynes (un) generally give the products of substitution $[Pt_2(\mu\text{-}Cl)_2Me_2(un)_2]$, but $CF_3C{\equiv}CCF_3$ gives insertion into the PtMe bond. Reaction of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ with ethylene yields the dimethyl(ethylene)platinum(II) complex *cis*-$[PtMe_2(SMe_2)(C_2H_4)]$ and with carbon monoxide *cis*-$[PtMe_2(SMe_2)(CO)]$ is formed. Oxidative addition of iodomethane to *cis*-$[PtMe_2(CO)(SMe_2)]$ produces a rare example of a platinum(IV) carbonyl complex *fac*-$[PtIMe_3(SMe_2)(CO)]$.

Introduction

This paper reports the synthesis, characterization, and properties of several compounds containing *cis*-methyl(ethylene)platinum(II) or *cis*-methylcarbonylplatinum(II) units. Such compounds are unusual, although some interesting examples such as *cis*-$[PtMe(C_2H_4)(diars)]^+$, diars = 1,2-$(Me_2As)_2C_6H_4$, and *cis*-$[PtMe_2(CO)_2]$ are known[1–3] and are of interest as models for catalytic intermediates.[4–6] This work was developed from an observation that reaction

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[1] Clark, H. C.; Jablonski, C. R.; von Werner, K. *J. Organomet. Chem.* **1974**, *82*, C51. Chisholm, M. H.; Clark, H. C. *Inorg. Chem.* **1973**, *12*, 991.

[2] Kuyper, J.; van der Laan, R.; Jeanneaus, F.; Vrieze, K. *Transition Met. Chem.* (*Weinheim, Ger.*) **1976**, *1*, 199.

[3] Anderson, G. K.; Clark, H. C.; Davies, J. A. *Inorg. Chem.* **1981**, *20*, 1636.

[4] Hartley, F. R. In *Comprehensive Organometallic Chemistry*; Abel, E. W.; Stone, F. G. A.; Wilkinson, G., Eds.; Pergamon: Oxford, 1982; Chapter 39.

[5] Clark, H. C.; Jain, V. K. *Coord. Chem. Rev.* **1984**, *55*, 151.

[6] Anderson, G. K.; Cross, R. J. *Acc. Chem. Res.* **1984**, *17*, 67.