Effects of isolobal substitution in cyclopentadienyl ligands: the azacyclopentadienyl system C_4R_4N. Comparative photoelectron spectra of the tetra-tert-butyl ferrocene derivatives *

Christoph Janiak [a], Norbert Kuhn [b] and Rolf Gleiter [c]

[a] *Institut für Anorganische und Analytische Chemie, Technische Universität Berlin, Straße des 17. Juni 135, 10623 Berlin (Germany)*
[b] *Fachbereich Chemie der Technischen Universität Chemnitz-Zwickau, Straße der Nationen 62, 09111 Chemnitz (Germany)*
[c] *Organisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 270, 69120 Heidelberg (Germany)*

Abstract

The He(I) photoelectron (PE) spectra of tetra-tert-butylferrocene (7) and tetra-tert-butyl-diazaferrocene (8) are reported. A comparison with the PE spectrum of ferrocene and pyridine reveals that (i) the hyperconjugative donor effect of a tert-butyl group is about twice that of a methyl or trimethylsilyl group, (ii) the electron-withdrawing potential of the nitrogen atom is very similar to that of the phosphorus atom in diphosphaferrocenes, (iii) there is no significant interaction between the nitrogen lone-pair orbitals. An explanation for the marked instability of diazaferrocenes compared to stable diphosphaferrocenes is offered. The PE spectra of 7 and 8 could be reproduced with an INDO/S theoretical calculation.

Key words: Iron; Isolobal; Azacyclopentadienyl; Ferrocene; Azaferrocene; Photoelectron spectroscopy

1. Introduction

The isolobal substitution [1–3] in **1** leads from the carbocyclic cyclopentadienyl (**2**) to the heterocyclic element-cyclopentadienyl system (**3**) which are then also isolobally related.

1

2   **3**
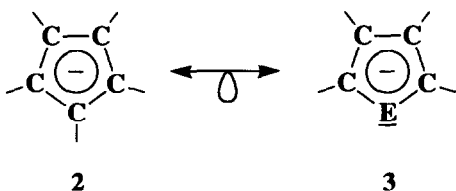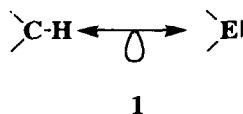
Heterocyclic analogs of metallocenes and half-sandwich compounds have become the focus of research in recent years and a variety of metal complexes with substituted derivatives of **3** are known (E = N [4–8], P [9,10], As [11], Sb [12], Bi [13]). Most attention has been paid to phosphacyclopentadienyl complexes, however, more and more examples of azacyclopentadienyl derivatives have now been synthesized [4–8]. This is especially remarkable as the prototypical 1,1'-diazaferrocenes (**4**) were for many years regarded as incapable of existence [4,14]. Stabilization of this structural type was eventually achieved, *e.g.* through bulky 2 and 5 substituents (**5**) [5,6].


4   **5**   **6**
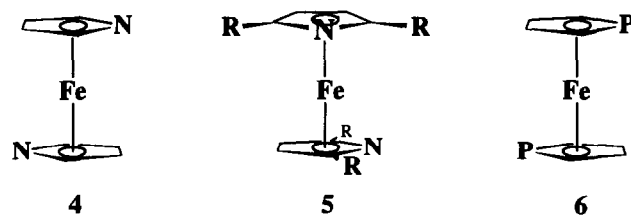
There is, however, still a marked difference in stabil-

Correspondence to: Dr. C. Janiak.
* Dedicated to Prof. Dr. E. O. Fischer on the occasion of his 75th birthday.

ity between, for example, diazaferrocenes and the stable diphosphaferrocenes (6) [9]. For a better understanding of the electronic effects of the isolobal substitution $2 \to 3$ with $E = N$, we present and discuss here the photoelectron spectra of iron complexes of 2 and 3, namely the tetra-tert-butyl substituted ferrocene and the diazaferrocene analog, $(C_5H_3{}^tBu_2)_2Fe$ (7) [15] and $(C_4H_2{}^tBu_2N)_2Fe$ (8) [6].

7

8
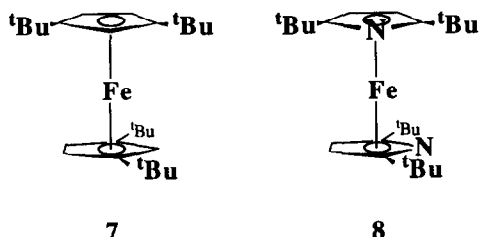
2. Results and discussion

The He(I) photoelectron spectra of 7 and 8 are shown in Fig. 1. The spectrum of ferrocene, taken from the literature [16–18] is included for comparison together with a pictorial assignment of the orbitals which most likely [19*] give rise to the ion states. The features in the spectra of 7 and 8 are discussed in correlation with the spectrum of ferrocene and pyridine [20]. In addition an INDO/S theoretical calculation was carried out on 7 and 8 following the work of Zerner et al. [21]. These results are compiled in Tables 1 and 2.

2.1. Electron donation by the tert-butyl group

The electron donating effect of the four tert-butyl groups causes the ionization energies (IE) of tetra-tert-butylferrocene (7) to be generally less than those of ferrocene. From the shift in the IEs when going from the spectrum of ferrocene to that of 7 in Fig. 1, it is evident that the four tert-butyl groups in 7 lower the binding energies of the valence electrons by about 0.7 eV. The more the orbital is localized on the ligand (e_{1u}, e_{1g}), the greater is the effect of tert-butyl substitution (up to 0.8 eV). In a comparison between 1,1'-dimethylferrocene and decamethylferrocene, it was found that the inductive effect of ring substitution is additive [16], so we can assign an electron-donating effect of ca. 0.18 eV per tert-butyl group. This effect of the tert-butyl substituent on the π-system and the central metal has already been observed in substituted benzenes and is best explained through a hyperconjugative perturba-

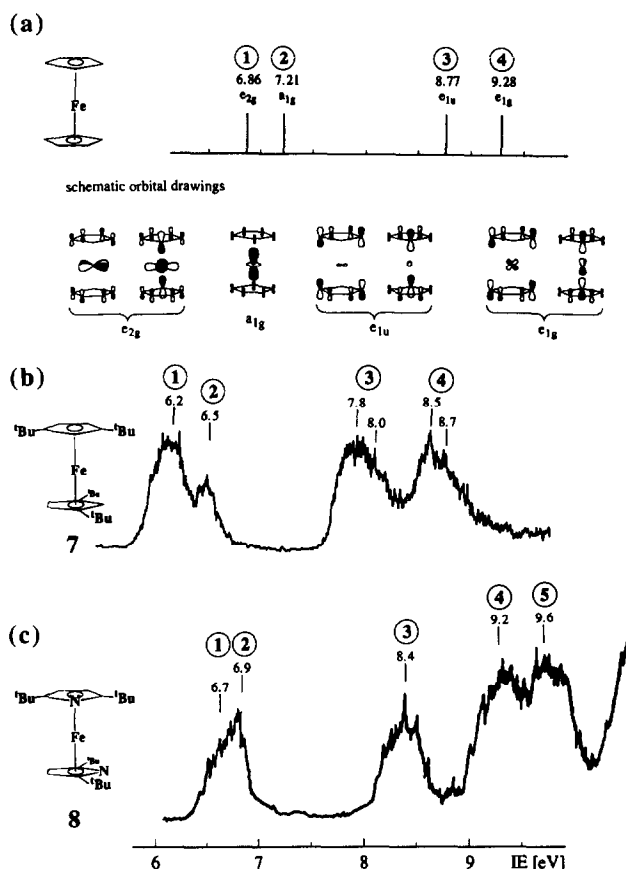* Reference number with asterisk indicates a note in the list of references.

Fig. 1. Low energy region of the He(I) photoelectron spectra of (a) ferrocene (with assignment and schematic orbital drawings), (b) tetra-tert-butylferrocene, 7, and (c) tetra-tert-butyl-diazaferrocene, 8. The encircled numbers are the band notations referred to in the text and in Tables 1 and 2. The spectrum of ferrocene was adopted from [16].

tion model [22]. The tert-butyl group is known to lower the ionization energies of π systems as a strong hyperconjugative donor through σ_{tBu}/π interactions [23]. In a quantitative comparison, a tert-butyl group can be considered to be roughly twice as electron donating as a methyl substituent (0.08 eV) [17] or a trimethylsilyl group (0.1 eV decrease in IE) [24].

2.2. Electron withdrawal by the nitrogen atom

The two ring nitrogens increase the binding energies of the valence electrons in 8 relative to 7 by 0.4–0.5 eV, i.e. 0.2–0.25 eV per nitrogen (see Fig. 1 or Tables 1 and 2). This change in ionization energies is very similar to what has been observed for 1,1'-diphosphaferrocene (6) [25]. Consequently, the comparative reactivities of diaza- and diphosphaferrocene with respect to their carbocyclic analogs should be similar, namely: (i) a lower reactivity towards electrophiles; (ii) decomposition upon attack by stronger electrophiles on

TABLE 1. Comparison between observed ionization energies (IE) and INDO/S calculated orbital energies for 7 and 8 [a]

Band no.	tetra-tert-Butyl-ferrocene, 7			tetra-tert-Butyl-diazaferrocene, 8		
	IE (eV)	$-\epsilon_i$ (eV)	Assignment [b]	IE (eV)	$-\epsilon_i$ (eV)	Assignment [b]
1	6.2	6.82	"e_{2g}"	6.7	7.64/7.78	"e_{2g}" } or { "a_{19}" [c]
2	6.5	7.30	"a_{1g}"	6.9	8.19	"a_{1g}" } or { "e_{29}"
3	{7.8 / 8.0}	8.20	"e_{1u}"	8.4	{8.44 / 8.50}	"e_{1u}" / "e_{1g}"
4	{8.5 / 8.7}	{8.89 / 9.05}	"e_{1g}"	9.2	{10.04 / 10.27}	"e_{1u}" / "e_{1g}"
5				9.6	10.75	N-lone-pairs

[a] Details on the calculational procedure as well as geometric parameters for 7 and 8 are given in the computational procedure section.

[b] The calculated orbital levels have been assigned using the symmetry labels from ferrocene (D_{5d}) despite the lower C_2 symmetry of 7 and 8. For a pictorial representation of the orbitals, see Fig. 1.

[c] Experimental assignment; see text, Section 2.5.

the heteroatom; and (iii) nucleophilic attack taking place at the heteroatom reflecting the high localization of the LUMO at this atom [9,25,26].

Finally, we note that the INDO/S method (see below) is capable of reproducing the observed difference in the orbital energies between 7 and 8 contrary to an extended Hückel study on ferrocene and diazaferrocene where the frontier orbitals were found to remain essentially invariant with respect to the isolobal substitution 2 to 3 [8].

2.3. The nitrogen lone-pair band

The band at 9.6 eV in the PE spectrum of 8 (No. 5) is assigned to an ionization from the nitrogen lone-pair orbitals (cf. Fig. 1, Tables 1 and 2) based on the N lone-pair binding energy in pyridine [20]. No splitting of the nitrogen lone-pair band can be observed, thus there appears to be no through-space or through-bond coupling [2,27] of the nitrogen atoms, as is often discussed for the heavier heterocyclopentadienyl [12,13] or more general heteroarene systems [28]. This is in agreement with a study on diazaferrocene [8], or even diphosphaferrocene [26] where no such N $\cdots$ N or P $\cdots$ P interaction, for example in the form of a conformational preference, was found. In comparison, the phosphorus lone-pair orbitals were assigned to bands

TABLE 2. Results from the ΔE(SCF) approximation for the lowest ion state [a]

Band no.	tetra-tert-Butylferrocene, 7			tetra-tert-Butyl-diaza ferrocene, 8		
	IE	$-\epsilon_i$ (eV)	ΔE(SCF)	IE	$-\epsilon_i$ (eV)	ΔE(SCF)
1	6.2	6.82	5.60	6.7	7.64	5.86

[a] ΔE(SCF) = E(ion) − E(neutral molecule).

at 10.15 and 10.35 eV from a PE study [25], somewhat lower than the band assigned to the P lone-pair in phosphinine (phosphabenzene) at 9.8–10.0 eV [29].

The nitrogen and even the phosphorus lone-pair orbitals are too contracted and too low in energy for an effective overlap with a high lying valence orbital of the central metal (cf. [8,26]) which is necessary for a through-bond effect and the directionality of the lone-pairs within the cyclopentadienyl ring planes (together with their contracted nature) makes them less susceptible for through-space coupling. Along these lines, we note that an interaction has been suggested between the antimony or bismuth atoms in 1,1'-distibaferrocenes [12] or 1,1'-dibismaferrocenes [13] based on X-ray structural investigations and also between the chlorine atoms in 1,1'-dichloroferrocene from a PE-spectral study [30]. The stronger coupling effects in these complexes can be reasoned by the higher-lying, more diffuse, and of course larger antimony and bismuth orbitals and by the out-of-plane orientation of the nonbonding chlorine p orbitals.

2.4. The instability of diazaferrocenes

Concerning the noted instability of unsubstituted diazaferrocenes compared to ferrocene and to the stable diphosphaferrocenes, we point out that the binding energies are increased in 8 relative to 7 (see Section 2.2). Therefore, the iron–aza-Cp bond would be thermodynamically more stable than the corresponding Fe–Cp interaction, so that the difference in stability must be of kinetic origin. In comparison to the diphosphaferrocenes, the higher energy N lone-pair position, its contracted nature and the higher p character of the N lone-pair orbital relative to the P lone-pair indicate an increased reactivity of the nitrogen, i.e. there is a relatively low barrier of reaction to even more stable complexes, rendering diazaferrocene a labile system

[31]. While the phosphorus atom in π complexes of the phospholyl anion has only a very low nucleophilicity [9,26], σ coordination is much more pronounced in the case of the pyrollyl anions, unless the non-bonding electron pair on the nitrogen atom is effectively blocked, *e.g.* through steric overcrowding of the α-positions (5) [32*].

2.5. INDO / S theoretical calculations

Zerner *et al.* [21] have employed an intermediate neglect of differential overlap method with spectroscopic parametrization (INDO/S) in electronic calculations on the ferrocene molecule. Following this work, we have used the semi-empirical INDO/S method here in the calculation of the PE spectra of 7 and 8. The results are given in Tables 1 and 2.

The ionization energies of the ferrocene derivatives have been evaluated by Koopmans' theorem [33] as the negative of the eigenvalues of the ground state MOs of the neutral molecules [34*] (Table 1). In addition, the lowest ionization energy has been calculated by making a separate calculation of the ion and subtracting this energy from the neutral species (this is termed the ΔE(SCF) approximation) (Table 1).

It can be seen from Tables 1 and 2 that the energies of the molecular orbitals based on a calculation of the neutral species deviate 1.2 eV or less from the observed ionization potentials [21]. A comparison of the INDO/S calculated orbital sets (energy as well as composition) in Table 1 supports a very similar electronic structure of 7 and ferrocene with respect to the orbital level ordering. In both (ionized) compounds, the first two bands stem from the almost pure metal MOs, $e_{2g} \equiv d_{xy}$, $d_{x^2-y^2}$ and $a_{1g} \equiv d_{z^2}$ with $e_{2g} < a_{1g}$, while the third and fourth band originate from the ligand localized MOs e_{1u} and e_{1g}. Thus, while the sequence of ionization potentials in 7 is the same as that agreed upon for the ferricinium ion, namely $e_{2g} < a_{1g} < e_{1u} < e_{1g}$ [16–19*,36], we note a higher complexity in the spectrum of 8. Experimentally, a very close proximity of the "e_{2g}" and "a_{1g}" band is found in 8 (Nos. 1 and 2) and from the relative intensities, we rather suggest the ordering "a_{1g}" $\leq$ "e_{2g}". In addition "e_{1u}" and "e_{1g}" in 8 show an increased splitting and are distributed over bands 3 and 4.

3. Conclusions

The PE spectra of tetra-tert-butylferrocene and te-tra-tert-butyl-diazaferrocene have been evaluated in comparison with the PE spectrum of ferrocene and pyridine. From the spectral changes it is deduced that (i) the hyperconjugative donor strength of a tert-butyl group is about twice the size of a methyl or trimethylsi-

lyl group, (ii) the electron withdrawing potential of the nitrogen atom is very similar to that of the phosphorus atom in diphosphaferrocenes, and (iii) there is no significant interaction between the N lone-pair orbitals. Furthermore, the instability of the iron–aza-Cp bond is not of thermodynamic but of kinetic origin due to the localization and high reactivity of the non-bonding nitrogen electrons.

4. Experimental details

The preparation of 7 and 8 is described in the literature [6,15]. The PE spectra of these two compounds were recorded on a PS-18 photoelectron spectrometer (Perkin-Elmer Ltd., Beaconsfield) at 120°C. The spectra were calibrated with Ar (15.76 eV, 15.94 eV) and Xe (12.13 eV, 13.44 eV). A resolution of 20 meV on the Ar-line $^2P_{3/2}$ was obtained.

5. Computational procedure

LCAO-MO-SCF calculations using the INDO/S approximation with spectroscopic parametrization [21,37] have been performed on tetra-tert-butyl-ferrocene (7) and tetra-tert-butyldiazaferrocene (8) and the lowest energy state of the respective ferricinium ions.

Since there is evidence that interatomic distances of a ferrocene derivative are not greatly changed in the vapour phase [38] or in the ion [39], the average solid state interatomic distances of Fe–C = 206.4, C–C = 140.9 and C–H = 96 pm in 7 [15] and Fe–C/N = 206.7, C–C/N = 144.9, C–H = 96 pm in 8 [6], respectively, have been used as restraints for both the neutral molecule and cation in an INDO/1 optimized geometry. The closed-shell, neutral molecule was treated in a restricted Hartree–Fock (RHF) mode, while the open-shell ion was calculated in the unrestricted (UHF) mode. An electron-correlation calculation on the ground state of ferrocene did not lead to appreciable changes in total or orbital energies [21].

Calculations were performed with the HyperChem computational package (Version 3.0, Autodesk Inc., Sausolito, CA 94965, USA) installed on a PC-80486/DX-33 computer.

References and notes

1 R. Hoffmann, *Angew. Chem.*, **94** (1982) 725; *Angew. Chem., Int. Ed. Engl.*, **21** (1982) 711.

2 T.A. Albright, J.K. Burdett and M.H. Whangbo, *Orbital Interactions in Chemistry*, Wiley, 1985, p. 802ff.

3 C. Elschenbroich and A. Salzer, *Organometallics*, 2nd edition, VCH Weinheim, 1992, p. 396ff.

4 Review: N. Kuhn, *Bull. Soc. Chim. Belg.*, **99** (1990) 707.

5 N. Kuhn, J. Kreutzberg, E.-M. Lampe, D. Bläser and R. Boese, *J. Organomet. Chem.*, **458** (1993) 125; N. Kuhn, S. Stubenrauch, R. Boese and D. Bläser, *J. Organomet. Chem.*, **440** (1992) 289; N. Kuhn, G. Henkel and S. Stubenrauch, *J. Chem. Soc., Chem. Commun.*, (1992) 760; N. Kuhn, G. Henkel and S. Stubenrauch, *Angew. Chem.*, **104** (1992) 766; *Angew. Chem., Int. Ed. Engl.*, **31** (1992) 778; N. Kuhn, M. Köckerling, S. Stubenrauch, D. Bläser and R. Boese, *J. Chem. Soc., Chem. Commun.*, (1991) 1368.

6 N. Kuhn, K. Jendral, R. Boese and D. Bläser, *Chem. Ber.*, **124** (1991) 89.

7 H. Schumann, J. Winterfeld, H. Hemling and N. Kuhn, *Chem. Ber.*, **126** (1993) 2657.

8 N. Kuhn, G. Henkel, J. Kreutzberg, S. Stubenrauch and C. Janiak, *J. Organomet. Chem.*, **456** (1993) 97.

9 Review: F. Mathey, *New J. Chem.*, **11** (1987) 585.

10 F. Nief, L. Ricard and F. Mathey, *Polyhedron*, **12** (1993) 19.

11 A.J. Ashe III, S. Mahmoud, C. Elschenbroich and M. Wünsch, *Angew. Chem.*, **99** (1987) 249; *Angew. Chem., Int. Ed. Engl.*, **26** (1987) 229.

12 A.J. Ashe III, T.R. Diephouse, J.W. Kampf and S.M. Al-Taweel, *Organometallics*, **10** (1991) 2068.

13 A.J. Ashe III, J.W. Kampf, D.B. Puranik and S.M. Al-Taweel, *Organometallics*, **11** (1992) 2743; A.J. Ashe III, J.W. Kampf and S.M. Al-Taweel, *J. Am. Chem. Soc.*, **114** (1992) 372.

14 F. Seel and V. Sperber, *J. Organomet. Chem.*, **14** (1968) 405.

15 T. Leigh, *J. Chem. Soc.*, (1964) 3294; Z.L. Kaluski, A.I. Gusev, A.E. Kalinin and Y.T. Struchkov, *Zh. Strukt. Khim.*, **13** (1972) 950; R. Boese, D. Bläser, N. Kuhn and S. Stubenrauch, *Z. Kristallogr.*, **205** (1993) 282.

16 C. Cauletti, J.C. Green, M.R. Kelly, P. Powell, J.v. Tilborg, J. Robbins and J. Smart, *J. Electron Spectrosc. Relat. Phenom.*, **19** (1980) 327.

17 S. Evans, M.L.H. Green, B. Jewitt, A.F. Orchard and C.F. Pygall, *J. Chem. Soc., Faraday Trans. 2*, **68** (1972) 1847.

18 J.W. Rabalais, L.O. Werme, T. Bergmark, L. Karlsson, M. Hussain and K. Siegbahn, *J. Chem. Phys.*, **57** (1972) 1185; erratum, **57** (1972) 4508.

19 For a controversy on the assignment of the nature of the cationic hole states, compare refs. 16–18 with N. Rösch and K.H. Johnson, *Chem. Phys. Lett.*, **24** (1974) 179.

20 See for example: E. Heilbronner, V. Hornung, F.H. Pinkerton and S.F. Thames, *Helv. Chim. Acta*, **55** (1972) 289.

21 M.C. Zerner, G.H. Loew, R.F. Kirchner and U.T. Mueller-Westerhoff, *J. Am. Chem. Soc.*, **102** (1980) 589.

22 W. Kaim, H. Tesmann and H. Bock, *Chem. Ber.*, **113** (1980) 3221;

H. Bock, W. Kaim and H.E. Rohwer, *Chem. Ber.*, **111** (1978) 3573.

23 C.G. Pitt, *J. Organomet. Chem.*, **61** (1973) 49; H. Bock and B.G. Ramsey, *Angew. Chem.*, **85** (1973) 773; *Angew. Chem., Int. Ed. Engl.*, **12** (1973) 734; and refs. therein.

24 P.G. Gassman, P.A. Deck, C.H. Winter, D.A. Dobbs and D.H. Cao, *Organometallics*, **11** (1992) 959.

25 C. Guimon, D. Gonbeau, G. Pfister-Guillouzo, G. de Lauzon and F. Mathey, *Chem. Phys. Lett.*, **104** (1984) 560.

26 N.M. Kostic and R.F. Fenske, *Organometallics*, **2** (1983) 1008.

27 R. Gleiter and W. Schäfer, *Acc. Chem. Res.*, **23** (1990) 369; M.N. Paddon-Row and K.D. Jordan, in J.F. Liebmann and A. Greenberg (eds.), *Modern Models of Bonding and Delocalization*, VCH Weinheim, 1988, p. 115; H.-D. Martin and B. Mayer, *Angew. Chem., Int. Ed. Engl.*, **22** (1983) 283; M.N. Paddon-Row, *Acc. Chem. Res.*, **15** (1982) 245; R. Gleiter, *Angew. Chem., Int. Ed. Engl.*, **13** (1974) 696; R. Hoffmann, *Acc. Chem. Res.*, **4** (1971) 1; R. Hoffmann, A. Imamura and W. Hehre, *J. Am. Chem. Soc.*, **90** (1968) 1499.

28 C. Elschenbroich, F. Bär, E. Bilger, D. Mahrwald, M. Nowotny and B. Metz, *Organometallics*, **12** (1993) 3373.

29 C. Batich, E. Heilbronner, V. Hornung, A.J. Ashe III, D.T. Clark, U.T. Cobley, D. Kilcast and I. Scanlan, *J. Am. Chem. Soc.*, **95** (1973) 928.

30 T. Vondrák, *J. Organomet. Chem.*, **275** (1984) 93.

31 J.E. Huheey, *Inorganic Chemistry*, 3rd edition, Harper and Row, New York, 1983, p. 547ff.

32 Compare the difference in the synthesis of bis(η^6-pyridine)chromium and bis-(η^6-phosphinine)vanadium; the former was only successful after blocking the α-positions by trimethylsilyl groups: C. Elschenbroich, J. Koch, J. Kroker, M. Wünsch, W. Massa, G. Baum and G. Stork, *Chem. Ber.*, **121** (1988) 1983; C. Elschenbroich, M. Nowotny, B. Metz, W. Massa and J. Graulich, *Angew. Chem.*, **103** (1991) 601; *Angew. Chem., Int. Ed. Engl.*, **30** (1991) 547.

33 T. Koopmans, *Physica*, **104** (1934) 1.

34 We are aware that in the case of organo-transition metal complexes, very often Koopmans' approximation is not valid. Ferrocene, in particular, was one of the first examples where the breakdown of Koopmans' theorem was demonstrated [35]. However, the spectroscopic parametrization employed in the INDO/S method resulted in a rather large reduction of relaxation energy and Koopmans' theorem was found to give a correct order of ionization potentials [21].

35 M.C. Böhm, *Z. Naturforsch.*, **37a** (1982) 12193 and refs. therein.

36 M.-M. Coutiere, J. Demuynck and A. Veillard, *Theor. Chim. Acta*, **27** (1972) 281.

37 A.D. Bacon and M.C. Zerner, *Theor. Chim. Acta*, **53** (1979); M.C. Zerner, in K.B. Lipkowitz and D.B. Boyd (eds.), *Reviews in Computational Chemistry II*, VCH, Weinheim, 1991, p. 313.

38 R.K. Bohn and A. Haaland, *J. Organomet. Chem.*, **5** (1966) 470.

39 P. Zanello, A. Cinquantini, S. Mangani, G. Opromella, L. Pardi, C. Janiak and M.D. Rausch, *J. Organomet. Chem.*, **471** (1994) 171.