

TETRACYANOETHYLENE COMPLEXES OF MONOMETHYLCYCLOPENTADIENYLCOBALT DERIVATIVES

M.J. MACAZAGA, M.S. DELGADO* and J.R. MASAGUER

*Departamento de Química Inorgánica, Universidad Autónoma de Madrid, Cantoblanco,
 Madrid-28049 (Spain)*

(Received February 17th, 1986)

Summary

The complexes (MeCp)Co(L)TCNE (L = CO, PPh₃, P(OMe)₃, py; MeCp = methylcyclopentadienyl; TCNE = tetracyanoethylene; py = pyridine) have been made. The TCNE acts as a one-electron oxidizing agent, and is σ -bonded to cobalt through a nitrile nitrogen. All the compounds have been characterized by elemental analysis, magnetic susceptibility measurements, and IR, electronic, ¹H NMR, and ESR spectroscopy.

Introduction

The coordination compounds formed between basic transition metal complexes and various π acids have been extensively studied [1,2]. These reactions are of interest because of their resemblance to fundamental steps in homogeneous catalytic processes [3,4]. As model compounds for the intermediate in these reactions, cyanoolefin complexes of transition metals have been the subject of many preparative and structural studies [5]. However, relatively few such complexes of cobalt(I) have been made [6,7].

Numerous complexes containing highly activated olefins, such as TCNE (tetracyanoethylene), are known, mainly Rh^I, Ir^I, Cr⁰ and Pt⁰ complexes [8–10]. Each of these complexes exhibits a single C \equiv N stretching vibration which may be regarded as diagnostic of π -olefin type metal–TCNE bonding. TCNE charge-transfer complexes are also known [11], and in some cases complete charge transfer with formation of TCNE radical anion has been demonstrated [12,13].

In another type of TCNE-complex the TCNE ligand acts as an oxidizing agent and is σ -bonded to metal through a nitrile nitrogen; e.g. (Cp)₂VXTCNE (X = Cl, Br, I) [14], (dppe)₂FeTCNE (dppe = diphenylphosphinoethane) [15] and SnX₂-(TCNE)THF (X = Cl, Br, I) [16].

In a TCNE complex of cyclopentadienylcobalt, CpCo(PMe₃)TCNE, reported by Werner et al., the TCNE ligand is π -bonded to cobalt (ν (C \equiv N) 2230 cm⁻¹) [17].

Previously we described the complexes (MeCp)Co(L)TCNE (L = CO, PPh₃), which do not undergo oxidative addition with XCN (X = Br, I) [18].

Magnetic susceptibility measurements and IR, UV-VIS and ESR spectroscopic studies on these complexes enable recognition of the way in which the TCNE is coordinated to cobalt. This type of study was carried out frequently with the analogous complexes having L = P(OMe)₃ or pyridine (py).

Discussion of results

Addition under N₂ of a benzene solution of TCNE to a solution of (MeCp)Co(CO)P(OMe)₃ in the same solvent results in loss of CO and precipitation of a black solid with the stoichiometry (MeCp)CoP(OMe)₃TCNE. The complex (MeCp)Co(py)TCNE was obtained from (MeCp)Co(CO)TCNE and pyridine in boiling benzene.

The complex (MeCp)CoP(OMe)₃TCNE and the previously reported (MeCp)Co(L)TCNE (L = CO, PPh₃) were also obtained by carrying out some reactions in THF. The complexes are soluble in this solvent and the reactions were monitored by IR spectroscopy (the initial $\nu(\text{CO})$ band disappeared and new bands due to TCNE ligand appeared). The reactions were complete when an equimolar amount of the TCNE had been added.

All the compounds are very hygroscopic and are sparingly soluble in weakly polar solvents (CH₂Cl₂, benzene) and very soluble in polar solvents (CH₃CN, DMF, DMSO).

Their IR spectra show the characteristic bands of the η -MeCp ring [19,20]. For the complex (MeCp)Co(CO)P(OMe)₃, the $\nu(\text{CO})$ band (1937 cm⁻¹) is typical of a terminal ligand [20].

The spectra of the complexes (MeCp)Co(L)TCNE (L = CO, PPh₃, P(OMe)₃, py) were obtained for Nujol mulls, KBr pellets, and acetone, THF, DMF and DMSO solutions. The $\nu(\text{C}\equiv\text{N})$ frequencies are listed in Table 1.

The spectra of (MeCp)Co(L)TCNE (L = CO, PPh₃) in Nujol mulls, show two bands. The one at lower frequency is broad, but is resolved in solution; the resolution becomes better as the polarity of the solvent is increased (Fig. 1), and four bands can be observed. The spectra of (MeCp)Co(L)TCNE (L = P(OMe)₃, py) display four bands either in Nujol or in solution.

CNDO/2 calculations on TCNE, TCNE⁻ and TCNE²⁻ indicate that electron density enters a π -MO which is antibonding with respect to each of the C \equiv N bonds

TABLE 1

$\nu(\text{C}\equiv\text{N})$ STRETCHING FREQUENCIES FOR THE COMPLEXES (in cm⁻¹)

	MeCpCo(CO)TCNE	MeCpCo(PPh ₃)TCNE	MeCpCo[P(OMe) ₃]TCNE	MeCpCo(py)TCNE
Nujol	222vs, 2175vs br	2218vs, 2160vs,br	2215s,sh, 2199vs 2177s,sh, 2155s,sh	2213s,sh, 2198vs 2178m,sh, 2160w,sh
THF	2220vs, 2198w 2173s,sh, 2160vs	2218vs, 2198vs 2175m,sh, 2163m,sh	2216s,sh, 2199vs 2177s,sh, 2158m	
DMSO	2218vs, 2198vs 2174vs, 2160vs	2216m,sh, 2198vs 2176s, 2163s	2216s,sh, 2199vs 2179m, 2162m	2213s,sh, 2198vs 2180s, 2160w,sh

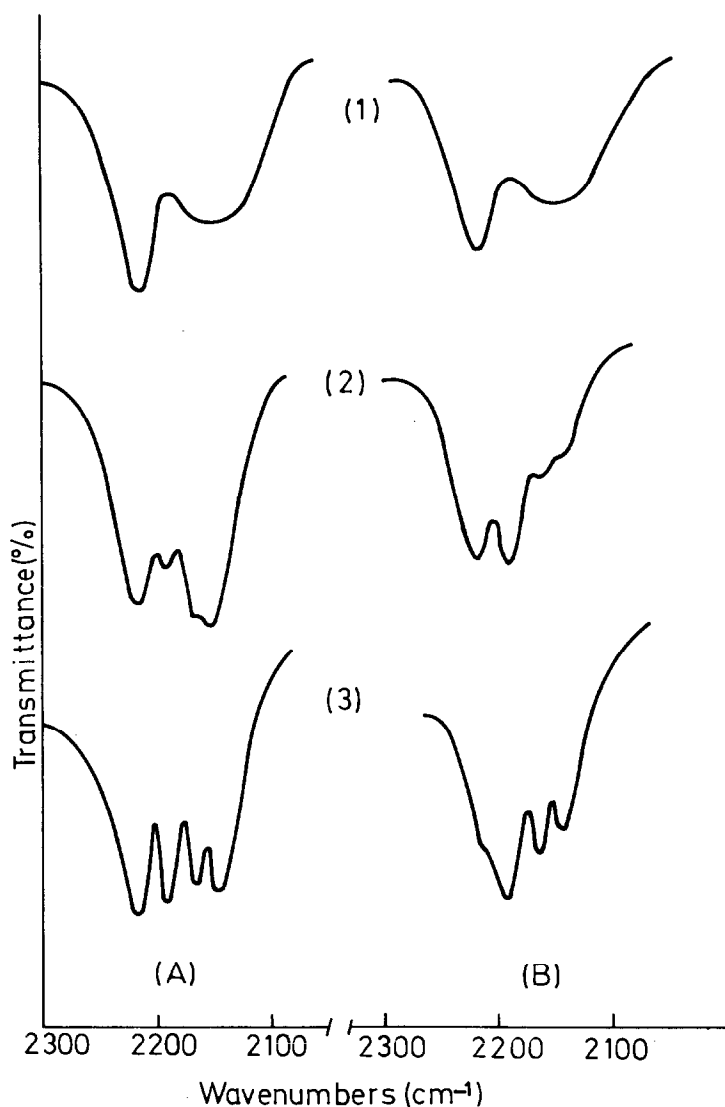


Fig. 1. $\nu(\text{C}\equiv\text{N})$ stretching frequencies for the complexes $(\text{MeCp})\text{Co}(\text{CO})\text{TCNE}$ (A), $(\text{MeCp})\text{Co}(\text{PPh}_3)\text{TCNE}$ (B) in Nujol mulls (1), THF (2) and DMSO (3) solution.

and also with respect to the central $\text{C}=\text{C}$ bond. Thus a lowering of $\nu(\text{C}\equiv\text{N})$ and $\nu(\text{C}=\text{C})$ frequencies is expected if the TCNE acts as an electron acceptor. In all the complexes the $\nu(\text{C}\equiv\text{N})$ is, in fact, lowered with respect to that in free TCNE (2260, 2225 cm^{-1}). The multiplicity of $\nu(\text{C}\equiv\text{N})$ bands is consistent with a low (local) symmetry of the coordinated TCNE, indicating that the TCNE is σ -bonded to cobalt through a *N*-nitrile [14,15]. The $\nu(\text{C}=\text{C})$ vibration, which should be observed below 1570 cm^{-1} (free TCNE), must be masked by MeCp ring vibrations.

Magnetic susceptibility measurements on the complexes $(\text{MeCp})\text{Co}(\text{L})\text{TCNE}$ ($\text{L} = \text{CO}, \text{PPh}_3$) show they are paramagnetic (μ_{eff} 1.98 and 2.08 MB, respectively).

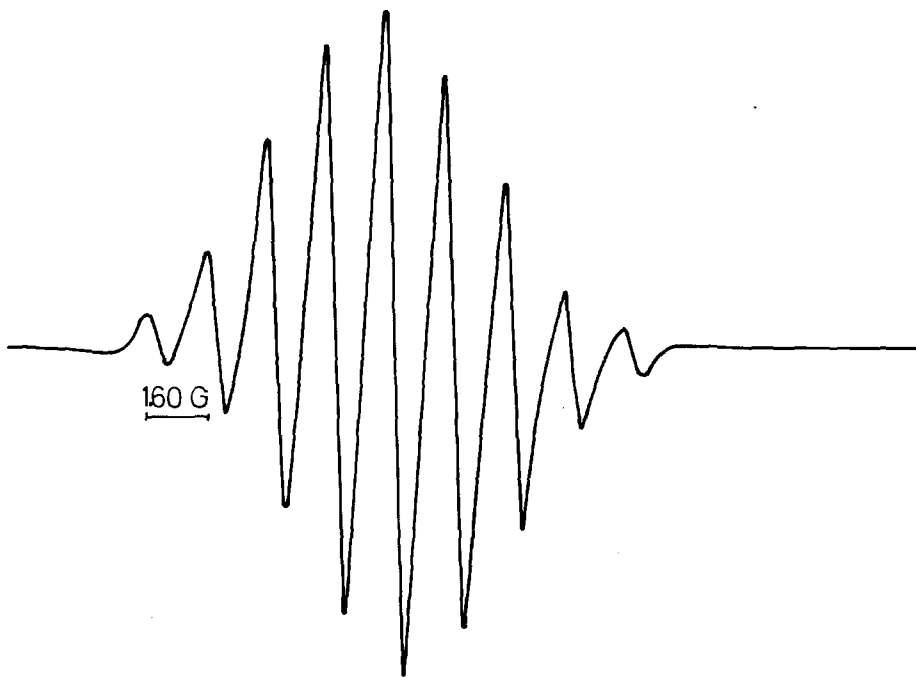


Fig. 2. ESR spectra for the complexes (MeCp)Co(L)TCNE (L = CO, PPh₃, P(OMe)₃, Py) in DMSO at 25°C.

The ESR spectra of all the complexes were obtained at room temperature in acetone, DMF and DMSO solutions. The spectra in the first two solvents confirm the paramagnetism but the broad signal observed shows no coupling to the ⁵⁹Co ($I = 7/2$) or the ¹⁴N ($I = 1$) nucleus. However, in DMSO solution the ESR spectra display a strong signal characteristic of TCNE anion radical (nine lines, a_N 1.60 G, $g = 1.998$) [21] (Fig. 2).

The electronic spectra were obtained in these same solvents, and were similar in all cases. A broad band was observed at λ_{\max} ca. 540 nm. In the 360–480 nm range, characteristic of TCNE anion radical [22], there are two broad bands, except for the complex (MeCp)Co(CO)TCNE which shows hyperfine structure (408, 416, 425, 435, 445, 456, 466 nm).

All the data obtained for the complexes (MeCp)Co(L)TCNE (L = CO, PPh₃, P(OMe)₃, py), indicates that the TCNE is reduced to TCNE⁻ and coordinates to cobalt through of one of the nitrile nitrogens. Thus the complexes can be regarded formally as (MeCp)CoL⁺·TCNE⁻, in which the cation has accepted σ -electron density from a nitrile nitrogen of TCNE⁻.

The observed values of μ_{eff} , which are smaller than those expected for two unpaired electrons, and the absence of a signal from TCNE⁻ in the ESR spectrum in acetone/DMF solutions, suggest that there is some interaction between the unpaired electron of Co^{II} (d^7) and the η -electron density on TCNE⁻. The ESR signal of TCNE⁻ which shows up in DMSO solutions and confirms this formulation for the complexes, probably appears because of the high ionizing power of this solvent.

Experimental

All the reactions were carried out under oxygen-free N_2 . The $(MeCp)Co(CO)_2$ was prepared by a published procedure [23]. The microanalyses were performed by the Dpto. Química Inorgánica de la Facultad de Ciencias de la Universidad de Alcalá de Henares (Madrid, Spain).

The IR spectra were recorded at $4000\text{--}200\text{ cm}^{-1}$ on a Nicolet 5 DX FT-IR spectrophotometer using Nujol mulls between CsI windows, KBr pellets, and acetone, THF, DMF and DMSO solutions. In all cases the solvent absorptions were subtracted by use of the spectrophotometer software. 1H NMR were recorded on a Bruker WM-200-SY. Magnetic susceptibilities were determined by the Gouy method.

The ESR spectra were recorded at a microwave frequency of 9 GHz (X-band) on a Varian E-12 spectrometer equipped with a HP 5342 A frequency meter and a Bruker NMR Gaussmeter. The electronic spectra were recorded on a Pye Unicam SP 8-100 spectrophotometer.

Preparation of $(MeCp)Co(CO)P(OMe)_3$

A solution of $(MeCp)Co(CO)_2$ (1.5 g, 7.7 mmol) and $P(OMe)_3$ (1.2 cm³, 10 mmol) in 25 cm³ benzene was held at the reflux temperature. The reaction was monitored by IR spectroscopy. After 5 h, the reaction was complete. (The $\nu(CO)$ initial: 2022, 1957 cm^{-1} disappeared and a new strong band at 1937 cm^{-1} was observed). The solvent and the residual $P(OMe)_3$ was removed under vacuum to leave a deep red oil. (Found: Co, 20.15. calcd.: Co, 20.32%). $\nu(CO)$ 1937 cm^{-1} . 1H NMR ($CDCl_3$): δ 1.65 (s, CH_3); 3.56 (d, $P(OMe)_3$); 4.55 (m, AA' of AA'BB'X for substituted Cp); 4.95 (m, BB' of AA'BB'X for substituted Cp) ppm.

Preparation of $(MeCp)CoP(OMe)_3TCNE$

A solution of TCNE (0.45 g, 3.5 mmol) in 30 cm³ benzene was slowly added dropwise to a solution of $(MeCp)Co(CO)P(OMe)_3$ (1 g, 3.5 mmol) in benzene (10 cm³) saturated with oxygen-free N_2 . A black solid immediately appeared, and evolution of CO was observed. The solid was filtered off, washed with hexane, and dried in vacuum. The yield was quantitative. (Found: C, 46.80; H, 4.20; N, 14.25; Co, 14.98. $C_{15}H_{16}CoO_3N_4P$ calcd.: C, 46.16; H, 4.10; N, 14.36; Co, 15.11%. 1H NMR ($CDCl_3$): δ 1.65 (s, CH_3); 3.75 (d, $P(OMe)_3$); 5.25 (m, AA' of AA'BB'X for substituted Cp); 5.42 (m, BB' of AA'BB'X for substituted Cp) ppm.

Preparation of $(MeCp)Co(py)TCNE$

A benzene solution (30 cm³) of $(MeCp)Co(CO)TCNE$ (1.4 g, 5.0 mmol) and pyridine (0.6 cm³, 7.4 mmol) was kept under reflux for 3 h. The black solid which separated was filtered off, washed with hexane, and dried in vacuum. The yield was quantitative. (Found: C, 59.40; H, 3.90; N, 20.02; Co, 16.85. $C_{17}H_{13}N_5Co$ calcd.: C, 59.13; H, 3.76; N, 20.24; Co, 17.02%). 1H NMR ($CDCl_3$): δ 1.67 (s, CH_3); 3.60–3.90 (m, py) ppm.

Acknowledgements

We thank Prof. C. Sieiro for the ESR spectra and for helpful comments and express our great appreciation of financial support from the Comisión Asesora de Investigación Científica y Técnica (Spain) (Project no. 0476/81).

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