Zirconium Complexes with the Trifunctional 3-Cyanopentane-2,4-dionate Ligand

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Five zirconium complexes containing the 3-cyanopentane-2,4-dionate and 2-cyano-1-phenylbutane-1,3-dionate ligands (L) have been prepared: $[ZrCl_2(C_6H_6NO_2)_2]$, $[ZrCl_2(C_{11}H_8NO_2)_2]$, $[ZrCl(C_6H_6NO_2)_3]$, $[Zr(C_6H_6NO_2)_4]$, and $[Zr(\eta-C_5H_5)(C_6H_6NO_2)_3]$. Infrared data shows that all β-diketonate ligands are co-ordinated to the metal centre through both oxygens; however, in complexes of the type $[ZrCl_2L_2]$ and $[ZrClL_3]$ the cyano-group appears to be co-ordinated as well.

THE synthesis of 3-cyanopentane-2,4-dione (2-acetylacetoacetonitrile) was first reported in 1898 by Traube.[1] The compound has a pK_a of 3.5 (pK_a = 9.0 for pentane-2,4-dione [2]) and exists entirely as the enol tautomer [3] (keto : enol = 20 : 80 for pentane-2,4-dione [4]). While a voluminous number of β-diketonate–metal complexes have been synthesized and characterized,[5] few studies of 3-cyanopentane-2,4-dionate–metal complexes have been reported. In 1962 Fackler [6] published the preparation of 12 oxygen-chelated complexes; a detailed examination of the position of the C≡N stretching frequency led to the conclusion that the π electrons of the 3-cyanopentane-2,4-dionate chelate ring are not strongly affected by overlap with the metal 3*d* orbitals. Furthermore, the i.r. spectra indicated that the cyano-groups were not interacting with any metal centres. In 1965 Cox *et al.*[7] reported the preparation of tris(3-cyanopentane-2,4-dionato)titanium(III) and bis(3-cyanopentane-2,4-dionato)oxotitanium(IV); these complexes exhibited no unusual properties such as C≡N co-ordination relative to the pentane-2,4-dionate analogues. Additionally, the tris(3-cyanopentane-2,4-dionato)-complexes of iron(III) [8] and manganese(III) [9] and the bis complex of copper(II) [10] have been reported; again no unusual properties were found. The sodium and potassium salts of 3-cyanopentane-2,4-dione have also been reported.[6,11,12] Finally, equilibrium constants of beryllium(II), copper(II), cobalt(II), and nickel(II) complexes with 3-cyanopentane-2,4-dione have been determined in 75% v/v dioxane–water.[13]

In 1973 we reported the first 3-cyanopentane-2,4-dionato-complexes for which strong evidence exists that the cyano-group is co-ordinated to a metal as well as the two oxygens of the enolate anion.[14] These complexes have the empirical formula $[MCl_3(C_6H_6NO_2)]$, M = Ti or Sn, $C_6H_6NO_2$ = oxygen-chelated 3-cyanopentane-2,4-dionate anion. The i.r. spectra (both in the cyano- and metal–halogen stretching regions) provide clear evidence that the 3-cyanopentane-2,4-dionate ligand is co-ordinated not only through both oxygens but through the cyano-group as well, *i.e.* the 3-cyanopentane-2,4-dionate anion is behaving as a bridging planar trifunctional ligand. A cyclic tetrameric structure was postulated for these complexes which is consistent with the tendency of titanium and tin to adopt a co-ordination number of six with an octahedral-based geometry.

With our results showing an unusual co-ordinative interaction for the 3-cyanopentane-2,4-dionate anion, we thought that it would be interesting to look at the zirconium tetrachloride–3-cyanopentane-2,4-dione system since zirconium exhibits co-ordination numbers of seven and eight in addition to six with β-diketonate ligands.[15] In particular, we were interested in attempting to synthesize complexes of the type $[ZrCl_x(C_6H_6NO_2)_{4-x}]$ and looking for unusual structures involving the uncommon planar trifunctional co-ordination of the 3-cyanopentane-2,4-dionate ligand. Reported herein are the preparation and characterization of several complexes derived from the reactions of zirconium tetrachloride and bis(η-cyclopentadienyl)zirconium dichloride with 3-cyanopentane-2,4-dione.

EXPERIMENTAL

Reagents and General Techniques.—Anhydrous reactor grade zirconium tetrachloride (Alfa) and dichlorobis(cyclopentadienyl)zirconium(IV) (Apache) were used as purchased. Pentane-2,4-dione and 1-phenylbutane-1,3-dione were obtained from Aldrich and Eastman, respectively, and used without further purification. Triethylamine (Eastman) was distilled from barium oxide under nitrogen prior to use. Benzene and 'hexanes' (Fisher) were distilled over calcium hydride; dichloromethane was distilled over phosphorous pentaoxide. All solvents were stored over Molecular Sieves (Linde 4-A) under nitrogen.

All operations in the synthesis of the metal complexes were conducted under anhydrous conditions (dry nitrogen and/or vacuum) in glass-ware patterned after Kontes Airless-Ware designed by Shriver.[16] Samples for analysis elemental, m.p., i.r., n.m.r.) were prepared in a Vacuum Atmospheres Dri-Lab under nitrogen.

Preparation of 3-*Cyanopentane*-2,4-*dione.*—The title compound was prepared along the lines of the synthesis presented by Fackler with the following modifications. We found it convenient to carry out the cyanogenation in the well known Brown hydrogenation apparatus.[17] Cyanogen was generated using 4 mol dm^{-3} sodium cyanide and an aqueous slurry of copper sulphate pentahydrate at room temperature. This technique allows ready monitoring of the course of the reaction. Final purification of the product was accomplished by vacuum sublimation at *ca.* 40 °C; this yielded well defined colorless crystals. Yields of *ca.*

50% based on pentane-2,4-dione were obtained. M.p. 53—54° (lit.,[1] 50 °C); ν(C≡N) = 2 219 cm^{-1}; δ(OH) = −16.59 p.p.m., δ(CH$_3$) = −2.42 p.p.m.

Preparation of 2-*Cyano*-1-*phenylbutane*-1,3-*dione*.—This compound was prepared in essentially the same manner as 3-cyanopentane-2,4-dione. The crude product that formed was first recrystallized from an ethanol–water system. The white crystals were then dissolved in a small volume of dichloromethane to which anhydrous magnesium sulphate was added. After filtering and evaporation of the solvent, the solid residue was sublimed *in vacuo* to give a 25% yield. M.p. 71—73 °C; ν(C≡N) = 2 221 cm^{-1}; δ(OH) = −17.44 p.p.m., δ(CH$_3$) = −2.47 p.p.m. (Found: C, 71.5; H, 4.80. Calc. for $C_{11}H_9NO_2$: C, 70.6; H, 4.85%).

Synthesis of Dichlorobis(3-*cyanopentane*-2,4-*dionato*)-*zirconium*(IV).—A 100-cm^3 three-necked round-bottom flask equipped with a magnetic stirrer, a nitrogen inlet, and a 25-cm^3 dropping funnel was charged with 7.94 g (34.1 mmol) of zirconium tetrachloride in the dry box. The system was then removed to the bench, and the reaction run under a nitrogen atmosphere using a safety bubbler. Using a syringe, 50 cm^3 of dichloromethane was transferred to the round-bottom flask, and a solution of 3-cyanopentane-2,4-dione (4.26 g, 34.0 mmol) in 25 cm^3 of dichloromethane was transferred to the dropping funnel. The zirconium tetrachloride slurry was cooled to 0 °C, and the ligand solution added dropwise. When addition was complete, the dropping funnel was replaced under a vigorous flow of nitrogen with a condenser topped with a second nitrogen inlet attached to the safety bubbler. The stopcock of the first nitrogen inlet was closed. The reaction mixture was refluxed 1.5 h. A small amount of white solid remained and was filtered off.

The slightly cloudy filtrate was reduced in volume to *ca.* 30 cm^3 with mild heating under reduced pressure. Then 50 cm^3 of hexanes were added whereupon a substantial amount of white solid precipitated. The volume of the mixture was further reduced to *ca.* 50 cm^3. The product was filtered and dried *in vacuo* at room temperature. M.p. 236—238 °C with some prior decomposition [Found: C, 34.8; H, 3.30; Cl, 17.25; Zr, 22.4. Calc. for $ZrCl_2(C_6H_6NO_2)_2$: C, 35.1; H, 2.95; Cl, 17.3; Zr, 22.25%].

Synthesis of Dichlorobis(2-*cyano*-1-*phenylbutane*-1,3-*dionato*)*zirconium*(IV).—This compound was synthesized in a manner similar to that described immediately above. 2-Cyano-1-phenylbutane-1,3-dione (2.31 g, 12.4 mmol), dissolved in 25 cm^3 of dichloromethane, was added dropwise to anhydrous zirconium tetrachloride (2.34 g, 10.0 mmol) slurried in 50 cm^3 of dichloromethane at 0 °C. The reaction mixture was then refluxed for 1.5 h. The solid remaining after reflux was removed by filtration, and the filtrate was reduced in volume under reduced pressure at room temperature to *ca.* 25 cm^3. Hexanes (60 cm^3) were added whereupon a substantial amount of white product formed. The precipitate was filtered, washed with hexanes, and dried *in vacuo* at room temperature. M.p. 192—194 °C with some prior decomposition [Found: C, 49.55; H, 3.35; Cl, 13.05; Zr, 17.25. Calc. for $ZrCl_2(C_{11}H_8NO_2)_2$: C, 49.45; H, 3.00; Cl, 13.25; Zr, 17.05%].

Synthesis of Chlorotris(3-*cyanopentane*-2,4-*dionato*)-*zirconium*(IV).—3-Cyanopentane-2,4-dione (3.03 g, 24.2 mmol), dissolved in 25 cm^3 of dichloromethane, was added dropwise to a slurry of zirconium tetrachloride (3.14 g, 13.5 mmol) in 50 cm^3 of dichloromethane at 0 °C. The resulting mixture was refluxed for 1.5 h and filtered. The cloudy filtrate was kept under nitrogen at 5 °C overnight. Additional precipitate formed and was filtered off. After allowing this second filtrate to stand several hours at room temperature, additional solid precipitated; subsequently, all the solvent was evaporated *in vacuo* at room temperature. The solid residue which remained was suspended in *ca.* 40 cm^3 of a 1 : 1 dichloromethane—hexanes mixture. The undissolved solid was removed by filtration, and on standing the filtrate yielded a significant amount of additional solid which was filtered off, washed with hexanes, and dried as above. M.p. 238—240 °C with some prior decomposition [Found: Cl, 7.25; Zr, 17.9. Calc. for $ZrCl(C_6H_6NO_2)_3$: Cl, 7.10; Zr, 18.3%].

Synthesis of Tetrakis(3-*cyanopentane*-2,4-*dionato*)-*zirconium*(IV).—*Method* 1. Impure chlorotris(3-cyanopentane-2,4-dionato)zirconium(IV) (1 g, 2 mmol) was added to 50 cm^3 of water and stirred for 2 h. The product was filtered in air, washed with water, and dried *in vacuo* at 80 °C. M.p. 273—276 °C (lit.,[18] 258.5 °C) [Found: C, 49.15; H, 4.20; Cl, 0.15; Zr, 15.8. Calc. for $Zr(C_6H_6NO_2)_4$: C, 49.05; H, 4.10; Cl, 0.00; Zr, 15.5%].

Method 2. 3-Cyanopentane-2,4-dione (3.55 g, 28.4 mmol), dissolved in 25 cm^3 of dichloromethane, was added dropwise to a slurry of zirconium tetrachloride (1.54 g, 6.61 mmol) in 50 cm^3 of dichloromethane at 0 °C. The reaction mixture was then refluxed for 4 h. The solid remaining after reflux was removed by filtration. The filtration was reduced to 25 cm^3 under reduced pressure. Hexanes (50 cm^3) were added, whereupon a white solid formed. It was isolated in the standard manner. M.p. 273—275 °C [Found: Zr, 15.45. Calc. for $Zr(C_6H_6NO_2)_4$: Zr, 15.5%].

Synthesis of Tris(3-*cyanopentane*-2,4-*dionato*)η-*cyclopentadienylzirconium*(IV).—3-Cyanopentane-2,4-dione (3.31 g, 26.5 mmol) was dissolved in 25 cm^3 of benzene containing triethylamine (1.87 cm^3, 13.4 mmol). This solution was then added dropwise to a solution of dichlorobis(η-cyclopentadienyl)zirconium(IV) (3.91 g, 13.4 mmol) in 50 cm^3 of benzene at 0 °C. The resulting reaction mixture was stirred at room temperature for 47 h. The triethylammonium chloride was removed by filtration. Hexanes (45 cm^3) were added to the filtrate whereupon much white solid formed. The solid was isolated as previously described. M.p. 200—204 °C with some prior decomposition [Found: C, 52.5; H, 4.50; Zr, 16.7. Calc. for $Zr(\eta\text{-}C_5H_5)(C_6H_6NO_2)_3$: C, 52.25; H, 4.40; Zr, 17.25%].

Characterization Measurements.—All melting points were measured in sealed capillaries and are uncorrected. Infrared spectra were determined with a Perkin-Elmer model 457 spectrophotometer. The instrument was calibrated with atmospheric CO_2 having bands at 2 367 and 2 336 cm^{-1}. All products were examined as mulls in Nujol between potassium bromide plates. Proton n.m.r. spectra were obtained with a Hitachi-Perkin-Elmer R-20B spectrometer at 60 MHz at 35 °C. Samples were dissolved in $CDCl_3$ except where noted.

RESULTS AND DISCUSSION

One of our initial goals in looking at the zirconium tetrachloride–3-cyanopentane-2,4-dionate system was simply to extend the series of complexes within the Group 4 metals having the $[MCl_3(C_6H_6NO_2)]$ stoicheiometry. A second goal was to prepare more highly substituted zirconium–3-cyanopentane-2,4-dionate complexes, particularly, $[\mathrm{ZrCl_2(C_6H_6NO_2)_2}]$ and $[\mathrm{ZrCl(C_6H_6NO_2)_3}]$. Given the readily accessible co-ordination number of eight for zirconium(IV) even with ligands of substantial bite such as β-diketonate anions, we thought that in complexes with the stoicheiometry $[\mathrm{ZrCl_2(C_6H_6NO_2)_2}]$ and $[\mathrm{ZrCl(C_6H_6NO_2)_3}]$, the cyano-group of an oxygen-chelated $\mathrm{C_6H_6NO_2}$ ligand would interact at a second zirconium centre to produce unusual oligomeric complex structures containing planar trifunctional $\mathrm{C_6H_6NO_2}$ groups.

We were not successful in preparing the zirconium analogue of $[\mathrm{TiCl_3(C_6H_6NO_2)}]$ and $[\mathrm{SnCl_3(C_6H_6NO_2)}]$; reactions of zirconium tetrachloride and 3-cyanopentane-2,4-dione at a 1 : 1 mol ratio in dichloromethane, benzene, and hexanes failed to give the desired mono-substituted products. It appears that with zirconium relative to tin and titanium there is a dominant tendency to move from the mono- to more highly substituted products.

In a dichloromethane–hexanes system zirconium tetrachloride and 3-cyanopentane-2,4-dione react to give the di-, tri-, and tetra-substituted products $[\mathrm{ZrCl_2(C_6H_6NO_2)_2}]$, $[\mathrm{ZrCl(C_6H_6NO_2)_3}]$, and $[\mathrm{Zr(C_6H_6NO_2)_4}]$. The stoicheiometry of these products is, of course, not surprising. The pentane-2,4-dionate ($\mathrm{C_5H_7O_2}$) analogues have been prepared and well characterized.[15] The complex $[\mathrm{ZrCl_2(C_5H_7O_2)_2}]$ is a monomeric, six-co-ordinate complex with oxygen-chelated β-diketonate ligands, $[\mathrm{ZrCl(C_5H_7O_2)_3}]$ has a seven-co-ordinate structure, and $[\mathrm{Zr(C_5H_7O_2)_4}]$ is eight-co-ordinate. On the other hand, it may be of significance to point out that with acidic β-diketones such as hexafluoroacetylacetone and trifluoroacetylacetone only tetrasubstituted [Zr(diketonate)$_4$] complexes have been reported. Furthermore, these β-diketones react with zirconium tetrachloride in anhydrous organic solvents under mild conditions to give the tetrasubstituted products whereas $[\mathrm{Zr(C_5H_7O_2)_4}]$ cannot be prepared satisfactorily by the reaction of zirconium tetrachloride and an excess of pentane-2,4-dione under anhydrous conditions.[15b]

TABLE 1

C–N stretching frequencies observed in cyano-β-diketonate complexes of zirconium(IV) [a]

Compound	C–N stretching frequencies (cm^{-1})
3-Cyanopentane-2,4-dione	2 219
2-Cyano-1-phenylbutane-1,3-dione	2 220
$[\mathrm{ZrCl_2(C_6H_6NO_2)_2}]$	2 255, 2 222
$[\mathrm{ZrCl_2(C_{11}H_8NO_2)_2}]$	2 240, (2 261, 2 219) [b]
$[\mathrm{ZrCl(C_6H_6NO_2)_3}]$	2 253, 2 221
$[\mathrm{Zr(C_5H_5)(C_6H_6NO_2)_3}]$	2 222, (2 225, 2 219) [b]
$[\mathrm{Zr(C_6H_6NO_2)_4}]$	2 219

[a] Samples suspended between KBr plates as Nujol mulls. [b] Shoulders of main band.

Selected data from the i.r. spectra for $[\mathrm{ZrCl_2(C_6H_6NO_2)_2}]$, $[\mathrm{ZrCl(C_6H_6NO_2)_3}]$, and $[\mathrm{Zr(C_6H_6NO_2)_4}]$ are presented in Table 1. The appearance of intense bands [$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$ and $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$] in the region from 1 500 to 1 625 cm^{-1} clearly indicates the presence of oxygen-chelated 3-cyanopentane-2,4-dionate as expected. These bands are similar to those observed in $[\mathrm{TiCl_3(C_6H_6NO_2)}]$, $[\mathrm{SnCl_3(C_6H_6NO_2)}]$, and $[\mathrm{TiCl_2(C_6H_6NO_2)_2}]$.[14] However, perusal of the region where cyanide stretching occurs shows some interesting patterns. First, one notices that for $[\mathrm{Zr(C_6H_6NO_2)_4}]$, where zirconium has achieved its maximum expected co-ordination number, $\nu(\mathrm{C{\equiv}N})$ is 2 219 cm^{-1}, *i.e.* there is no shift relative to free 3-cyanopentane-2,4-dione. Also, we found for *cis*-$[\mathrm{TiCl_2(C_6H_6NO_2)_2}]$ where titanium is co-ordinatively saturated, that $\nu(\mathrm{C{\equiv}N})$ is 2 223 cm^{-1}. Thus, in view of Fackler's observations these results are consistent with $[\mathrm{Zr(C_6H_6NO_2)_4}]$ having an oxygen-chelated eight-co-ordinate structure without any co-ordination of the cyano-groups. If $[\mathrm{ZrCl_2(C_6H_6NO_2)_2}]$ has the same basic structure as $[\mathrm{ZrCl_2(C_5H_7O_2)_2}]$ {which is isostructural with $[\mathrm{TiCl_2(C_5H_7O_2)_2}]$}, then one would expect to observe an unshifted $\nu(\mathrm{C{\equiv}N})$ band near the frequency for free 3-cyanopentane-2,4-dione. However, observation of the spectrum for $[\mathrm{ZrCl_2(C_6H_6NO_2)_2}]$ shows two prominent bands in the cyanide stretching region. The band at 2 222 cm^{-1} is associated with a non-co-ordinating cyano-group while the band at 2 255 cm^{-1} ($\Delta\nu = 33$ cm^{-1}) indicates co-ordinated cyanide. From previous observations of nitrile complexation to metals, it is expected that co-ordination of the cyano-group in a 3-cyanopentane-2,4-dionate ligand would lead to both an increase in the energy and the intensity of the absorption.[19] Thus, for $[\mathrm{ZrCl_2(C_6H_6NO_2)_2}]$ it appears that only one of the two cyano-groups per empirical formula unit is co-ordinated to a second zirconium centre and so forth. The i.r. spectrum for $[\mathrm{ZrCl_2(C_{11}H_8NO_2)_2}]$ is more complicated but still suggests some cyano-group co-ordination.

A similar pattern is observed with $[\mathrm{ZrCl(C_6H_6NO_2)_3}]$ where $\nu(\mathrm{C{\equiv}N})$ bands are observed at 2 253 and 2 221 cm^{-1}. Again we see both co-ordinated and free cyano-groups. With this monomeric unit, however, only a single cyano-group needs to co-ordinate to the zirconium centre to complete the maximum expected co-ordination number of eight. Indeed, one notices that for $[\mathrm{ZrCl(C_6H_6NO_2)_3}]$ the intensity of the free cyano-band is now greater than that for the co-ordinated band which is consistent with one co-ordinated and two non-co-ordinated 3-cyanopentane-2,4-dionate ligands. At this point we do not know what the solid-state structures are.

Since η-cyclopentadienyltris(pentane-2,4-dionato)zirconium and chloro(η-cyclopentadienyl)bis(pentane-2,4-dionato)zirconium are readily synthesized and are six- and seven-co-ordinate (assuming η-$\mathrm{C_5H_5}$ occupies only one site), we undertook the synthesis of the 3-cyanopentane-2,4-dionate analogues. We were unsuccessful in preparing $[\mathrm{ZrCl(\eta\text{-}C_5H_5)(C_6H_6NO_2)_2}]$; however, we were able to prepare readily $[\mathrm{Zr(\eta\text{-}C_5H_5)(C_6H_6NO_2)_3}]$. Contrary to our hope to find trifunctional cyano-β-diketonate ligands, we observed only a single major C≡N band at 2 222 cm^{-1} with shoulders at 2 225 and 2 215 cm^{-1}. Thus, in this case the cyclopentadienyl group is either too large to allow another ligand into the co-ordination sphere or the η-C_5H_5 group reduces the Lewis activity of the zirconium.

TABLE 2

Proton chemical-shift data for zirconium β-diketonate complexes

Compound	δ(CH_3)[a] L = 3-cyanoacetylacetonate	δ(CH_3)[a] L = acetylacetonate
HL	−2.42	−2.04[b]
[$ZrCl_2L_2$]	−2.47, −2.43[c]	−2.14[b]
[$ZrClL_3$]	−2.45, −2.30[c]	−2.06[b]
[ZrL_4]	−2.31	−1.96[c]
[$Zr(C_5H_5)L_3$]	−2.34, −2.25, −1.99	−1.97, −1.89, −1.63[d]

[a] Measured in p.p.m. (±0.02) relative to an internal standard of $SiMe_4$: temperature 35 °C; solvent, except where noted, $CDCl_3$. [b] Ref. 15. [c] Solvent CH_2Cl_2. [d] J. J. Howe and T. J. Pinnavaia, *Synth. React. Inorg. Metal-Org. Chem.*, 1974, **4**, 325.

The methyl bands in the proton n.m.r. spectra of 3-cyanopentane-2,4-dione, [$ZrCl_2(C_6H_6NO_2)_2$], [$ZrCl(C_6H_6NO_2)_3$], and [$Zr(C_6H_6NO_2)_4$] are listed in Table 2. Although *cis*-[$ZrCl_2(C_6H_6NO_2)_2$] has two sets of non-equivalent methyl protons {assuming a monomeric solution structure similar to that of *cis*-[$ZrCl_2(C_5H_7O_2)_2$]}, only a single methyl resonance would be expected at 35 °C because of the observed lability of zirconium-β-diketonate systems. However, two peaks of unequal intensity are observed for a solution of [$ZrCl_2(C_6H_6NO_2)_2$] in CH_2Cl_2. We assign the high-field peak to [$ZrCl(C_6H_6NO_2)_3$] which may be formed by reaction (1).

$$3[ZrCl_2(C_6H_6NO_2)_2] \rightleftharpoons 2[ZrCl(C_6H_2NO_2)_3] + ZrCl_4 \quad (1)$$

This type of equilibrium appears to occur with $SiCl_2(C_5H_7O_2)_2$.[20] The low-field peak we assign to the [$ZrCl_2(C_6H_6NO_2)_2$] species. Similarly, when [$ZrCl(C_6H_6NO_2)_3$] is examined in CH_2Cl_2 two methyl peaks are evident. The high-field peak is assigned to [$Zr(C_6H_6NO_2)_4$] and the low-field peak to [$ZrCl(C_6H_6NO_2)_3$]. No peak due to [$ZrCl_2(C_6H_6NO_2)_2$] was observed. The complex [$Zr(C_6H_6NO_2)_4$] may be formed *via* the overall reaction (2).

$$4[ZrCl(C_6H_6NO_2)_3] \rightleftharpoons 3[Zr(C_6H_6NO_2)_4] + ZrCl_4 \quad (2)$$

Finally, [$Zr(C_6H_6NO_2)_4$] exhibits only the single CH_3 resonance expected.

Additional support for the assignments made above can be had by referring to the pentane-2,4-dionate series where the position of the methyl resonances moves upfield as the degree of substitution increases. For reasons which are not apparent the di- and tri-substituted products in the pentane-2,4-dionate series do not exhibit the equilibria seen above.

For [$Zr(\eta$-$C_5H_5)(C_6H_6NO_2)_3$] the proton n.m.r. spectrum in the methyl group region is consistent with observations on other [$Zr(\eta$-$C_5H_5)$(diketonate)$_3$] complexes.[21] These complexes have a basic pentagonal-bipyramidal structure with the centre of the η-C_5H_5 ring occupying an axial site. This geometry yields four non-equivalent methyl groups. However, at 35 °C only three resonances are observed. This has been ascribed to the fact that the equatorial methyl groups interchange rapidly by a 'low-temperature process' whereas the axial–equatorial ligand remains rigid until significantly higher temperatures.

A final note on the synthesis of these complexes is in order. All of the complexes described herein are readily synthesized in good yields except [$ZrCl(C_6H_6NO_2)_3$]. First of all the procedure by which we isolated this compound necessarily leads to low yields. The simple reaction of zirconium tetrachloride and 3-cyanopentane-2,4-dione in a 1 : 3 mol ratio, a reaction which works well for the analogous pentane-2,4-dionate system, gives a substantial amount of the tetrasubstituted product as an impurity. Furthermore, the basic method reported herein is prone to give either the tetra- or the di-substituted product as an impurity, *i.e.* the solvent volumes and ratios are extremely crucial and difficult to reproduce exactly.

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