

DICYCLOPENTADIENYLNICKEL-ALKYNE COMPLEXES: PHOTOCHEMICAL FORMATION AND MASS SPECTRA

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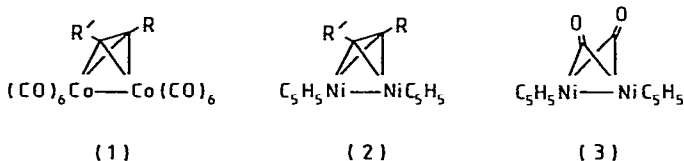
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Summary

Irradiation of toluene or n-hexane solutions of dicyclopentadienyldicarbonyl-dinickel complexes at $\lambda > 350$ nm gives good yields of bridged dinuclear complexes $(RC\equiv CR')(CpNi)_2$. Their bonding and mass spectra are discussed.

Among the vast array of compounds formed from Group VIII metal carbonyls and alkynes are a number of dinuclear metal complexes in which the alkyne carbons are bonded to both metal atoms [1]. Those (1) from octacarbonyldicobalt are formed easily at room temperature [2], whilst those (2) from dicyclopentadienyldicarbonyldinickel (3) are formed only on heating the components [3,4]. Although the latter reactions were successful when diarylalkynes were used [3–5], they gave lower yields with alkylalkynes [3] and failed to



give dinuclear metal complexes with other alkynes such as ethynedioic acid and its methyl ester [3,6]. We have shown that reactions between dicyclopentadienyldicarbonyldinickel and alkynes proceed smoothly under the influence of light to give dinuclear complexes even with alkynes which failed to do so in a thermal reaction. The structures of the new complexes have been established by spectroscopy and mass spectrometry.

Results

Since dicyclopentadienyldicarbonyldinickel (3) shows strong absorptions at 355 and 550 nm it seemed that a photochemical procedure might be successful,

for although the absorption bands of the diphenyl- and diperfluorophenyl complexes reach into the visible at ca. 470 and 660 nm they are of much lower intensity. In the event, when the nickel carbonyl (3) and alkynes were irradiated in deoxygenated toluene under nitrogen with a tungsten-halogen lamp using aqueous sodium nitrite as a filter ($\lambda > 390$ nm) smooth reactions ensued. The rates of reactions were substantially increased when stannic chloride in hydrochloric acid was used as a filter ($\lambda > 330$ nm). n-Hexane was found to be a better solvent than toluene insofar as reactions were notably faster and work-up was easier. Diarylethyne gave nearly quantitative yields with only molar equivalents of reagents. Dimethyl ethynedioate, propyn-1-ol and 1-acetoxyprop-2-yne had to be used in excess to produce best results. Although these latter reactions were slower, yields were still good and work-up was easy.

The last three alkynes gave rise to new complexes all of which are very dark-green solids giving rise to fairly air-stable green solutions. Thus, the alkynes were liberated only slowly when oxygen was bubbled through the solutions. Although the propyn-1-ol complex was obtained as a sharp-melting solid with the expected spectral data (see next section) we were unable to obtain a satisfactory elemental analysis for it. However, it was easily converted into the 1-acetoxyprop-2-yne complex with sodium acetate in acetic acid. We were not able to oxidise the hydroxyl group with mild oxidising agents such as manganese dioxide and pyridine dichromate; no reaction ensued.

Discussion

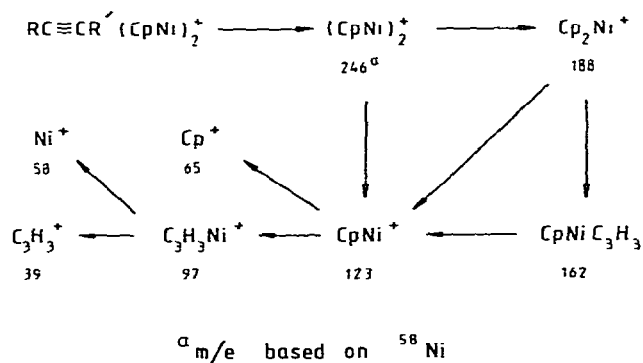
The tetrahedral array of the four central atoms together with the *cis*-bent geometry of the alkyne ligands has been established for a number of nickel complexes (2, R = R' = H, C₆H₅ and C₆F₅; R = CF₃, R' = P(O)(C₆H₅)₂) by X-ray crystallography [5,7–9]. It is clear from the spectral data to be presented that the new complexes have the same basic structure in which the degree of π -bonding between the alkyne and the nickel atoms is quite substantial. Thus, in addition to similar short wave bands all complexes display two characteristic absorptions in the visible one at 455–482 nm (ϵ ca. 2000) and another weaker one at 650–660 nm (ϵ ca. 1000).

For the dimethyl ethynedioate complex (2, R = R' = CO₂Me) the alteration of π -electron density in the triple bond of the alkyne when it is complexed is shown additionally in its IR spectrum. A band at 1715 cm⁻¹ in the complex is to be compared with one at 1730 cm⁻¹ for the alkyne and one at 1734 cm⁻¹ for diethyl *Z*-ethenedioate [10]. Since conjugation between the carbon–carbon triple bond and the carbonyl group as judged by IR spectra is about the same as that between the carbon–carbon double bond and the carbonyl group, the above result (1715 cm⁻¹) must indicate appreciable back bonding from the metal atoms.

For the propyn-1-ol (2, R = H; R' = CH₂OH) and the 1-acetoxyprop-2-yne (R = H; R' = CH₂OCOCH₃) complexes the olefinic character of the complexed alkynes is reflected in their NMR and IR spectra. Thus, the alkyne protons in the alcohol and acetate complexes show at δ 5.02 and 5.00 ppm respectively, values which contrast with δ ca. 2.50 ppm for the uncomplexed alkynes, but which are closely similar to those for the C(3) protons of allyl alcohol which

occur at δ 5.13 and 5.25 ppm [11]. Even greater deshielding of the alkyne protons is observed for the zero-valent platinum and cobalt complexes $L_2Pt-(RC\equiv CH)$ [12] and $(RC\equiv CH)Co(CO)_6$ [13] which show absorptions at δ 6.0–6.5 ppm. The methylene protons of the propyn-1-ol complex showing at δ 4.16 ppm as compared with δ 4.28 for the alkyne itself but similar to those in allyl alcohol which show at δ 4.13 ppm. Finally the strong $C_{sp}-H$ frequency at 3319 cm^{-1} shown by the alcohol and its acetate has given way to one at 2960 cm^{-1} in the complexes.

Since the physical constants of the alkyne moieties of the complexes so closely approximate to those of an uncomplexed alkene it is tempting to view these complexes as containing the equivalent of a bent *cis*-excited state of the alkyne [14], so that the valencebond structures depicted represent only connections between atoms rather than give any indications of the nature of the bonding. What is certain is that the metal–metal bonds are much stronger than the metal to bridging-carbon bonds; for aside from the lability of some of the complexes to oxygen when the alkyne can be recovered [3], the mass spectra of all complexes examined display (following a weak top *m/e*) an abundant ion corresponding to $(CpNi)_2^+$. The route(s) by which this ion breaks down as depicted below show a number of interesting points.



SCHEME 1

It is clear that the ion $(CpNi)_2^+$ can decompose in two ways. Cleavage of the Ni–Ni bond to give $CpNi^+$ (*m/e* 123), always an abundant ion, is an obvious route; more interesting is the extrusion of a nickel atom to give the dicyclopentadienylnickel ion (*m/e* 188). This latter ion is always an abundant one and is the base peak for the perfluorodiphenylethyne and propyn-1-ol complexes. Loss of the cyclopentadienyl radical could then lead to $CpNi^+$ (*m/e* 123). The strength of the nickel–carbon bonding in the dicyclopentadienylnickel ion (*m/e* 188) is displayed in the alternative manner in which this ion clearly does break down. It is evident that ethyne is lost to give the cyclopentadienylcyclopropenylnickel ion (*m/e* 162), the base peak for the propyn-1-ol complex. Loss of the cyclopropenyl radical would then lead to the cyclopentadienylnickel (*m/e* 123) or alternatively loss of the cyclopentadienyl radical would give $C_3H_3Ni^+$ (*m/e* 97). This ion which occurs in the spectra of all the complexes may well also derive from $CpNi^+$ (*m/e* 123) by the loss of ethyne. In conclusion it is worthy of note that the $4n + 2$ aromatic cyclopropenylium ion (*m/e* 39) is

always present in the mass spectrum of these compounds, whereas the $4n$ π -electron cyclopentadienylum ion is not present in any of them.

Experimental

μ -(Diphenylethyne)-bis(η^5 -cyclopentadienylnickel)

(a) *Thermal reaction.* A solution of dicyclopentadienyldicarbonylnickel (0.51 g, 1.68 mmol) and diphenylethyne (0.3 g, 1.68 mmol) in deaerated toluene (10 cm³) was refluxed under nitrogen for 2 h. The solution was filtered and the solvent evaporated. Chromatography of the residue on neutral alumina (20 g) using n-hexane/benzene (1/1) as eluent followed by recrystallisation from n-hexane/ether (4/1) gave the title compound as dark green needles (0.58 g, 82%), m.p. 148–149°C (Ref. [3] cites 149–150°C) (Found: C, 68.0; H, 4.9. C₂₄H₂₀Ni₂ calcd.: C, 67.7; H, 4.7%). λ_{\max} (n-hexane) 254, 354, 464 and 660 nm (ϵ 29050, 17930, 2008 and 982 respectively).

(b) *Photochemical reactions.* A solution of dicyclopentadienyldicarbonylnickel (0.051 g, 0.168 mmol) and diphenylethyne (0.030 g, 0.168 mmol) in deaerated toluene (3 cm³) was irradiated at 25°C with a tungsten-halogen lamp using 1 M sodium nitrite as a filter ($\lambda > 390$ nm). After 7 h the solution was filtered and evaporated. Recrystallisation of the residue from n-hexane/ether (4/1) gave the title compound as dark green needles (59 mg, 84%).

When the above experiment was repeated using 0.4 M stannic chloride in 1 M hydrochloric acid as filter ($\lambda > 350$ nm) the reaction was complete in 4 h, and the yield of pure product, m.p. 148–149°C, was 63 mg (90%).

When the above experiment was repeated using n-hexane as solvent and stannic chloride/hydrochloric acid as filter ($\lambda > 350$ nm) the reaction was complete in 2.5 h, and the yield of pure product was 65 mg (93%).

μ -(Diperfluorophenylethyne)-bis(η^5 -cyclopentadienylnickel)

(a) *Thermal reaction.* As previously reported [5].

(b) *Photochemical reaction.* A solution of dicyclopentadienyldicarbonylnickel (51 mg, 0.168 mmol) and diperfluorophenylethyne (60 mg, 0.168 mmol) in deaerated toluene (3 cm³) was irradiated under nitrogen at 25°C with light (> 350 nm). TLC monitoring (alumina, n-hexane) showed completion of reaction after 2 h. The solution was filtered and evaporated. Recrystallisation of the residue from n-hexane gave μ -(diperfluorophenylethyne)-bis(η^5 -cyclopentadienylnickel) as dark green needles (95 mg, 94%), m.p. 218–219°C (Ref. [5] cites m.p. 218–219°C) (Found: C, 47.9; H, 1.5; F, 31.4. C₂₄H₁₀F₁₀Ni₂ calcd.: C, 47.6; H, 1.65; F, 31.4%). λ_{\max} (n-hexane) 263, 308, 474 and 660 nm (ϵ 35860, 24260, 2426 and 1424 respectively).

μ -(Dimethylethyndioate)-bis(η^5 -cyclopentadienylnickel)

A solution of dicyclopentadienyldicarbonylnickel (75 mg, 0.24 mmol) and dimethyl ethyndioate (44 mg, 0.308 mmol) in deaerated n-hexane/toluene (9/1) (4 cm³) was irradiated at 25°C under nitrogen with light ($\lambda > 350$ nm). TLC monitoring (alumina, benzene) showed completion of reaction after 4 h. Work-up in the usual manner followed by preparative TLC, gave, after recryst-

tallisation from n-hexane, μ -(dimethylethyndioate)-bis(η^5 -cyclopentadienyl-nickel) as green needles (70 mg, 73%), m.p. 103°C (Found: C, 49.6; H, 4.2. $C_{16}H_{16}Ni_2O_4$ calcd.: C, 49.3; H, 4.1%). λ_{max} (n-hexane) 263, 315, 370, 482 and 650 nm (ϵ 13310, 11410, 19400, 1749 and 1369 respectively). ν_{max} (CCl_4) 2960m, 1715s, 1430m, 1250s and 1170s cm^{-1} . δ (CCl_4) 5.20 (10H, s) and 3.68 (6H, s) ppm.

μ -(Propyn-1-ol)-bis(η^5 -cyclopentadienylnickel)

A solution of dicyclopentadienyldicarbonyldinickel (150 mg, 0.494 mmol) and prop-2-yn-1-ol (84 mg, 0.616 mmol) and deaerated n-hexane (5 cm^3) was irradiated at 25°C under nitrogen with light ($\lambda > 350$ nm) for 10 h. Work-up in the usual manner followed by preparative TLC (benzene/chloroform 1/4) gave, after recrystallisation from n-hexane/ether (4/1), μ -(propyn-1-ol)-bis(η^5 -cyclopentadienylnickel) as a green microcrystalline solid (78 mg, 52%) m.p. 90–91°C. λ_{max} (cyclohexane) 228, 280, 300, 349, 455 and 650 nm (ϵ 14150, 7384, 7692, 21540, 2460 and 860 respectively). ν_{max} ($CHCl_3$) 3550m, 2960s, 2850s, 1360m, 1330m and 1000 cm^{-1} . δ ($CDCl_3$) 5.15 (1.0H, s), 5.02 (1H, s), 4.16 (2H, s) and 1.86 (1H, s, br).

μ -(1-Acetoxyprop-2-yne)-bis(η^5 -cyclopentadienylnickel)

A solution of dicyclopentadienyldicarbonyldinickel (151 mg, 0.50 mmol) and 1-acetoxyprop-2-yne (98 mg, 1.0 mmol) in deaerated n-hexane (5 cm^3) was irradiated under nitrogen at 25°C with light ($\lambda > 350$ nm) for 10 h. Work-up in the usual manner, including column chromatography on silica using first hexane/benzene (2/1) then benzene as eluent gave μ -(1-acetoxy-prop-2-yne)-bis(η^5 -cyclopentadienylnickel) as a green solid. Recrystallisation from n-hexane afforded dark-green needles (94 mg, 62%), m.p. 48.5–49°C (Found: C, 52.8; H, 4.35. $C_{15}H_{16}Ni_2O_2$ calcd.: C, 52.2; H, 4.6%). λ_{max} (n-hexane) 240, 278, 300, 350, 455 and 650 nm (ϵ 11080, 7580, 7870, 16320, 1865 and 845 respectively). ν_{max} (CCl_4) 2960m, 2930s, 2860m, 1745vs, 1370m, 1340m and 1250br cm^{-1} . δ (CCl_4) 5.22 (10H, s) 5.0 (3H, s) and 2.12 (3H, s) ppm.

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