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SYNTHESIS AND SOME REACTIONS OF
 η^5 -PENTAMETHYLCYCLOPENTADIENYLNICKEL COMPLEXES

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Summary

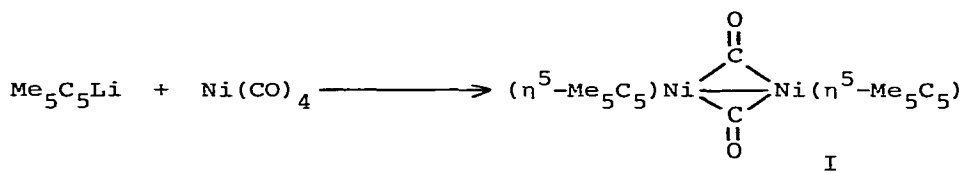
Reaction of $\text{Me}_5\text{C}_5\text{Li}$ and $\text{Ni}(\text{CO})_4$ gave $[(\eta^5\text{-Me}_5\text{C}_5)\text{Ni}(\text{CO})]_2$ (I) in 40 % yield. Reaction of I with iodine followed by addition of a tertiary phosphine or reaction of $(\text{PPh}_3)_2\text{NiX}_2$ with $\text{Me}_5\text{C}_5\text{Li}$ or $\text{Me}_5\text{C}_5\text{SnBu}_3$ gave $(\eta^5\text{-Me}_5\text{C}_5)\text{Ni}(\text{L})\text{X}$ (II) (L = tertiary phosphine, X = halogen). Treatment of II with RLi (R = Me, $\text{PhC}\equiv\text{C}$) afforded $(\eta^5\text{-Me}_5\text{C}_5)\text{Ni}(\text{L})\text{R}$ (III). The spectroscopic properties and the reactivities of η^5 -pentamethylcyclopentadienylnickel complexes indicate that the $\eta^5\text{-Me}_5\text{C}_5$ ligand is more electron-donating and a sterically more bulky than the $\eta^5\text{-C}_5\text{H}_5$ ligand.

Various metal complexes having a η^5 -pentamethylcyclopentadienyl($\eta^5\text{-Me}_5\text{C}_5$) ligand [1] are now known. However, no η^5 -pentamethylcyclopentadienylnickel complexes have been reported and attempts to prepare such complexes have not

yet been successful*. In order to compare the electronic and steric character of the $\eta^5\text{-Me}_5\text{C}_5$ and the $\eta^5\text{-C}_5\text{H}_5$ ligands in nickel complexes, we have tried to prepare some η^5 -pentamethylcyclopentadienylnickel complexes and report here their successful synthesis and a study of their properties.

Results and discussion

The reaction of lithium pentamethylcyclopentadienide with nickel tetracarbonyl in refluxing THF gave di- μ -carbonyl-bis(η^5 -pentamethylcyclopentadienylnickel) (I) in good yield**.



The ^1H NMR spectrum of I shows the signal due to the methyl protons of the $\eta^5\text{-Me}_5\text{C}_5$ ligand as a singlet at δ 1.75 ppm. The mass spectrum shows the molecular ion at m/e 442. The molecular weight and the isotopic pattern confirm the dinuclear structure of I. The physical properties of I are summarized in Table 1 and compared with those of the known $[(\eta^5\text{-C}_5\text{H}_5)\text{Ni}(\text{CO})]_2$. The IR bands of the bridging carbonyls appear at 1857 and 1815 cm^{-1} ; these frequencies are *ca.* 40 cm^{-1} lower than those of $[(\eta^5\text{-C}_5\text{H}_5)\text{Ni}(\text{CO})]_2$. The shift of the carbonyl absorptions to lower frequency may be attributed to

* Attempted reaction of $\text{Ni}(\text{CO})_4$ with acetylpentamethylcyclopentadiene gave negative results [2].

** The reaction of $\text{Me}_5\text{C}_5\text{H}$ with $\text{Ni}(\text{CO})_4$ in refluxing benzene only gave a trace of I. Formation of $[(\eta^5\text{-C}_5\text{H}_5)\text{Ni}(\text{CO})]_2$ from $\text{C}_5\text{H}_5\text{Na}$ and $\text{Ni}(\text{CO})_4$ has been claimed in a patent [3].

TABLE 1

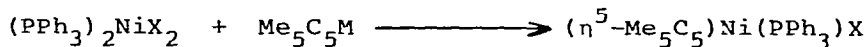
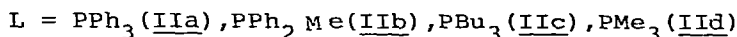
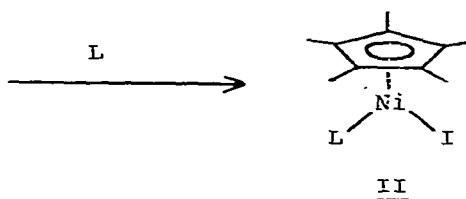
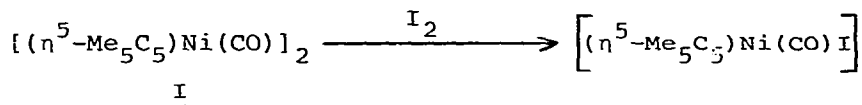
COMPARISON OF $[(\eta^5\text{-C}_5\text{H}_5)\text{Ni}(\text{CO})]_2$ AND $[(\eta^5\text{-MeC}_5\text{H}_4)\text{Ni}(\text{CO})]_2$ (I)

Compound	M.p. ^a (°C)	IR ^b ν_{CO} (cm^{-1})	λ_{max}^b (nm)	^{13}C NMR (δ , ppm) ^c
				CO R_5C_5 Me
$[(\eta^5\text{-C}_5\text{H}_5)\text{Ni}(\text{CO})]_2$	135-136	1855, 1896	496 ($\epsilon=5100$), 356 ($\epsilon=12400$)	226.2 93.9
$[(\eta^5\text{-MeC}_5\text{H}_4)\text{Ni}(\text{CO})]_2$	162-163	1815, 1857	522 ($\epsilon=4600$), 419 ($\epsilon=11400$)	238.3 101.3 9.3

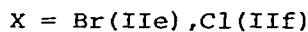
^a Measured in an argon-filled capillary tube. ^b Cyclohexane solution. ^c Solvent; CD_2Cl_2 , chemical shifts in ppm downfield from TMS.

the electron-donating character of the $\eta^5\text{-Me}_5\text{C}_5$ ligand, compared to that of the $\eta^5\text{-C}_5\text{H}_5$ ligand. Such a difference in electron-donating ability is also shown in the ^{13}C NMR and the electronic spectra. The carbonyl carbon signal appears at 238.3 ppm, shifted 12.1 ppm downfield from the carbonyl carbon chemical shift of $[(\eta^5\text{-C}_5\text{H}_5)\text{Ni}(\text{CO})]_2$. The λ_{max} of I shows a bathochromic shift. The observed shifts are consistent with the tendency [4,5] shown in the various transition metal carbonyl complexes which have electron-donating ligands and the magnitude of the shifts are remarkable.

According to the methods employed for the preparation of $\eta^5\text{-C}_5\text{H}_5$ analogues [6,7], $(\eta^5\text{-Me}_5\text{C}_5)\text{Ni}(\text{L})\text{X}$ (II) (L = tertiary phosphine, X = halogen) was obtained by the reaction of I with iodine in ether at -20°C , followed by addition of a tertiary phosphine, or by the reaction of $(\text{PPh}_3)_2\text{NiX}_2$ with $\text{Me}_5\text{C}_5\text{M}$ (M = Li, SnBu_3) in THF at room temperature.



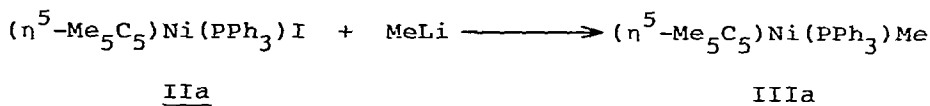
II



These complexes (IIa-IIf) are air-stable in the solid state, similar to the corresponding η^5 -cyclopentadienyl

derivatives. In the ^1H NMR spectra, the methyl protons of $\eta^5\text{-Me}_5\text{C}_5$ ligands of all these complexes show doublet resonances centered at δ 1.26-1.64 ppm ($J_{\text{PH}} = 1.4\text{-}1.7$ Hz).

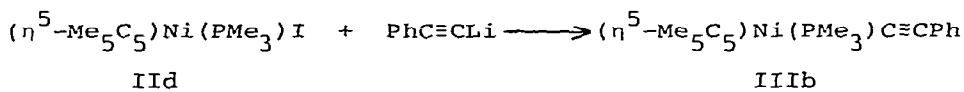
The complex $(\eta^5\text{-Me}_5\text{C}_5)\text{Ni}(\text{PPh}_3)\text{X}$ reacted with various organolithium reagents, but only $(\eta^5\text{-Me}_5\text{C}_5)\text{Ni}(\text{PPh}_3)\text{Me}$ (IIIa) was isolated [8].



Compound IV is unstable in air even in the solid state ;

$(\eta^5\text{-C}_5\text{H}_5)\text{Ni}(\text{PPh}_3)\text{Me}$ [8] is air-stable.

An air-stable Ni-C σ -bonded derivative, $(\eta^5\text{-Me}_5\text{C}_5)\text{Ni}(\text{PMe}_3)\text{-C}\equiv\text{CPh}$ (IIIb) was isolated from the reaction of IIId with $\text{PhC}\equiv\text{CLi}$.



The lack of success in the attempted preparation of $(\eta^5\text{-Me}_5\text{C}_5)\text{Ni}(\text{PPh}_3)\text{R}$ complexes, except IIIa, may be explained by destabilizing steric interactions between the triphenylphosphine ligand, the $\eta^5\text{-Me}_5\text{C}_5$ ligand, and the attacking nucleophile. The successful isolation of IIIb may be attributed to a decrease in steric hindrance.

The reactions of $(\eta^5\text{-C}_5\text{H}_5)\text{Ni}(\text{PPh}_3)\text{X}$ with an excess of PPh_3 easily give the corresponding ionic complexes, $[(\eta^5\text{-C}_5\text{H}_5)\text{Ni}(\text{PPh}_3)_2]^+$ [9], but IIa did not give an analogous ionic η^5 -pentamethylcyclopentadienyl derivative under similar conditions, although electronic factors should favor the formation of the ionic species. Our inability to prepare $[(\eta^5\text{-Me}_5\text{C}_5)\text{Ni}(\text{PPh}_3)_2]^+$ may be rationalized in terms of steric hindrance involving in this case two bulky phosphines and the $\eta^5\text{-Me}_5\text{C}_5$ ligand.

Experimental

All reactions were carried out under an argon or a nitrogen atmosphere. Tetrahydrofuran dried with benzophenone ketyl, ether and benzene dried over CaH_2 , were used. For column chromatography, Sumitomo Activated Alumina KCG-30 was used. Pentamethylcyclopentadiene was prepared by a literature method [10].

Melting points were uncorrected. ^1H NMR spectra were obtained using a Varian HA-100 or a JEOL C-60HL spectrometer in C_6D_6 . ^{13}C NMR spectra were recorded on a JEOL JNM-FX-100 spectrometer, operating in the Fourier transform mode at 25.16 MHz; CD_2Cl_2 was used as an internal lock. IR spectra were obtained using a Shimadzu IR-27G spectrometer and were calibrated with polystyrene bands. Electronic spectra were obtained using a Shimadzu UV-180 spectrometer. The mass spectrum was measured on a Nippondenshi JPS-1S mass spectrometer with direct inlet system at 75 eV.

Preparation of $[(\eta^5\text{-Me}_5\text{C}_5)\text{Ni}(\text{CO})]_2$ (I)

To a solution of pentamethylcyclopentadiene (4.2 ml, 25 mmol) in THF (200 ml) was added *n*-butyllithium (28 mmol) in hexane and the mixture was stirred for 1 hr. A solution of $\text{Ni}(\text{CO})_4$ (3.8 ml, 29 mmol) in THF (100 ml) was added dropwise to the resulting suspension of lithium pentamethylcyclopentadienide and the reaction mixture was refluxed for 10 hr. The color of the mixture changed to purple-red. The solvent was removed *in vacuo* and the residual solid was extracted with hexane until the hexane extracts no longer were colored. The extract was filtered, and the concentrated filtrate was chromatographed on alumina to give a purple-red band. Elution with ether and evaporation of the eluate left a purple-red solid. Sublimation of the residue at $120^\circ\text{C}/0.1\text{mm Hg}$ gave purple-red crystals of I (2.2 g, 40 %).

Preparation of $(\eta^5\text{-Me}_5\text{C}_5)\text{Ni(L)I}$ (II)

$(\eta^5\text{-Me}_5\text{C}_5)\text{Ni(PPh}_3\text{)I}$ (IIa) A solution of iodine (0.700 g, 2.76 mmol) in ether (40 ml) was added dropwise to a solution of I (1.226 g, 2.76 mmol) in ether (40 ml) at -20°C . The purple-red solution changed to a brown suspension. The mixture was stirred for 0.5 hr. Then, a solution of triphenylphosphine (1.450 g, 5.52 mmol) in benzene (50 ml) was added dropwise at the same temperature and the mixture was stirred until the temperature was raised to room temperature. The color of the mixture gradually turned maroon. The mixture was filtered and the solvent was evaporated. The resulting red-brown solid was recrystallized from benzene-hexane to give brown-red crystals of IIa (2.808 g, 87 %).

The same method was employed to the preparation of IIb-IIIc.

Preparation of $(\eta^5\text{-Me}_5\text{C}_5)\text{Ni(PPh}_3\text{)X}$ (IIe, IIf)

A solution of $\text{Me}_5\text{C}_5\text{SnBu}_3$ [11] (2.5 mmol) in THF was added to $(\text{PPh}_3)_2\text{NiBr}_2$ (1.86 g, 2.5 mmol) in THF (30 ml) and the mixture was stirred for 1 hr. The color of the mixture gradually changed from green to purple-red. The solvent was removed from the mixture. The residue was extracted with benzene and the extracts was filtered. The red filtrate was concentrated. After addition of hexane to the residue, the solution was kept in a refrigerator. Red crystals of IIe (0.91 g, 68 %) were obtained.

Similarly, IIf was prepared in 45 % yield. The use of $\text{Me}_5\text{C}_5\text{Li}$ instead of $\text{Me}_5\text{C}_5\text{SnBu}_3$ gave IIe and IIf in 12 % and 5 % yield, respectively.

Preparation of $(\eta^5\text{-Me}_5\text{C}_5)\text{Ni(PPh}_3\text{)Me}$ (IIIa)

Methyl lithium (10 mmol) in ether was added to an ice cooled benzene (100 ml) solution of IIa (1.166 g, 2.0 mmol)

TABLE 2

ANALYTICAL AND PHYSICAL DATA

Compound	Color	Yield (%)	M.p. ^a (°C)	Analysis				¹ H NMR (C ₆ D ₆) (δ, ppm)	
				found (calcd.) (%)	C	H	Halogen	Me ₅ C ₅	others
$[(\eta^5\text{-Me}_5\text{C}_5\text{Ni}(\text{CO}))_2]_2^b$	purple-red	40	162-163	59.54 (59.53)	6.89 (6.81)			1.75(s) ^c	
$(\eta^5\text{-Me}_5\text{C}_5\text{Ni}(\text{PPh}_3)_2\text{I})$	brown-red	87	196-198 ^d	57.68 (57.67)	5.19 (5.19)	21.75 (21.76)		1.47(d) ^e $J_{PH}=1.4\text{Hz}$	
$(\eta^5\text{-Me}_5\text{C}_5\text{Ni}(\text{PPh}_2\text{Me})\text{I})$	red	58	161-162	53.01 (53.02)	5.41 (5.42)	24.10 (24.35)		1.43(d) $J_{PH}=1.7\text{Hz}$	2.22(d, P-Me) ^{c, e} $J_{PH}=8.9\text{Hz}$
$(\eta^5\text{-Me}_5\text{C}_5\text{Ni}(\text{PBu}_3)_2\text{I})$	purple-red	55	66-67	50.33 (50.51)	8.14 (8.09)	23.60 (24.26)		1.64(d) $J_{PH}=1.5\text{Hz}$	0.7-1.9(m, PBu ₃) ^c
$(\eta^5\text{-Me}_5\text{C}_5\text{Ni}(\text{PMe}_3)_2\text{I})$	purple-red	30	117-118	39.48 (39.34)	6.12 (6.09)	32.03 (31.97)		1.57(d) $J_{PH}=1.7\text{Hz}$	1.07(d, PMe ₃) $J_{PH}=9.2\text{Hz}$
$(\eta^5\text{-Me}_5\text{C}_5\text{Ni}(\text{PPh}_3)\text{Br})$	red	68	209-211 ^d	62.67 (62.73)	5.64 (5.64)	14.93 (14.90)		1.33(d) ^e $J_{PH}=1.6\text{Hz}$	
$(\eta^5\text{-Me}_5\text{C}_5\text{Ni}(\text{PPh}_3)\text{Cl})$	red	45	177-178 ^d	68.34 (68.40)	5.97 (6.15)	7.21 (7.21)		1.26(d) ^e $J_{PH}=1.4\text{Hz}$	
$(\eta^5\text{-Me}_5\text{C}_5\text{Ni}(\text{PPh}_3)\text{Me})$	green	34	-130 ^f	73.58 (73.91)	7.05 (7.06)			1.64(s) $J_{PH}=6.0\text{Hz}$	-0.81(d, Me) ^{c, e}
$(\eta^5\text{-Me}_5\text{C}_5\text{Ni}(\text{PMe}_3)(\text{C}\equiv\text{CPh})_2\text{I})^g$	green	36	91-92	67.79 (67.96)	7.89 (7.88)			1.76(d) $J_{PH}=1.4\text{Hz}$	1.02(d, PMe ₃) $J_{PH}=9.6\text{Hz}$

^a Measured in an argon-filled capillary tube. ^b M⁺ (m/e): 442; ν_{CO} (cyclohexane): 1857, 1815 cm⁻¹.

^c 100MHz. ^d Melts with decomposition. ^e Phenyl proton resonances are omitted. ^f Decomposition.

^g ν_{C=C}: 2090 cm⁻¹ (benzene), 2080 cm⁻¹ (KBr).

and the mixture was stirred at room temperature. The color of the mixture slowly changed from maroon to greenish brown and after 18 hr to dark green. Then, aqueous ammonium chloride was added to the mixture in an ice-water bath. The green organic layer was separated and dried on sodium sulfate. Without concentration, this dried solution was chromatographed on alumina, eluting with benzene. A dark-green fraction was collected and the solvent was evaporated almost to dryness *in vacuo*. After addition of hexane (3 ml) to the residue, the solution was kept in a refrigerator. Dark green crystals of IIIa (0.322 g, 34 %) were obtained.

Preparation of $(\eta^5\text{-Me}_5\text{C}_5)\text{Ni}(\text{PMe}_3)(\text{C}\equiv\text{CPh})$ (IIIb)

To a solution of IIId (0.090 g, 0.23 mmol) in benzene (20 ml) was added $\text{PhC}\equiv\text{CLi}$ (0.23 mmol) prepared from *n*-BuLi in hexane and $\text{PhC}\equiv\text{CH}$ in ether and the mixture was stirred at room temperature. The mixture changed from purple-red to brown-yellow, then gradually to dark green in a 0.5 hr. The mixture was cooled to 0°C and aqueous ammonium chloride was added. The green organic layer was separated and dried on sodium sulfate in a short time. The dried solution was chromatographed on alumina, eluting with benzene. The dark green fraction was collected and removal of benzene *in vacuo* left a green solid. Recrystallization from hexane at ca. -30°C gave dark green crystals of IIIb (0.030 g, 36 %).

Physical data of all new complexes obtained here are summarized in Table 2.

References

- 1 R.B.King, *Coord. Chem Rev.*, 20 (1976) 155, and references cited therein.
- 2 R.B.King and A.Efraty, *J. Amer. Chem. Soc.*, 94 (1972) 3773.
- 3 H.Cordes, Ger. Patent 1,060,397, July 2, 1959 (Chem. Abst. 55, 8431d).
- 4 G.M.Bodner and L.J.Todd, *Inorg. Chem.*, 13 (1974) 1335.
- 5 P.S.Braterman, D. W.Milne, E.W.Randall, and E.Rosenberg, *J. Chem. Soc., Dalton*, (1973) 1027.
- 6 W.K.Schropp, *J. Inorg. Nucl. Chem.*, 24 (1962) 1688,1690.
- 7 R.J.Cross and R.Wardle, *J. Chem. Soc. (A)*, (1971) 2000.
- 8 H.Yamazaki, T.Nishido, Y.Matsumoto, S.Sumida, and N.Hagihara, *J. Organometal. Chem.*, 6 (1966) 86.
- 9 P.M.Treichel and R.L.Shubkin, *Inorg. Chim. Acta*, 2 (1968) 485.
- 10 D.Feitler and G.M.Whitesides, *Inorg. Chem.*, 15 (1976) 466.
- 11 M.J.Bunker, A.D.Cian, and M.L.H.Green, *J. Chem. Soc. Chem. Commun.*, (1977) 59.