Journal of Organometallic Chemistry, 178 (1979) 371—379

NICKELOCENE CHEMISTRY

II *. NEW METHYLIDYNE TRINICKEL CLUSTER COMPOUNDS

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(Received April 19th, 1979)

Summary

The new methylidene trinickel cluster complexes, [$RCNi_3(\eta^5\text{-}C_5H_5)_3$] (R = CMe_3 or $SiMe_3$) and [$Me_3SiCNi_3(\eta^5\text{-}C_5H_5)_2(\eta^5\text{-}C_5H_4CH_2SiMe_3)$] have been isolated in low yield from reactions between nickelocene and the corresponding alkyllithium reagents, RCH_2Li. The compounds [$RCNi_3(\eta^5\text{-}C_5H_5)_3$] (R = Ph, CMe_3 or $SiMe_3$) have also been obtained by treatment of the σ-alkylnickel complexes [$(\eta^5\text{-}C_5H_5)Ni(CH_2R)(PPh_3)$] with n-BuLi in the presence of an excess of nickelocene, but under similar conditions [$(\eta^5\text{-}C_5H_5)Ni(CH_2C_{10}H_7\text{-}2)(PPh_3)$] (where $C_{10}H_7$-2 = 2-naphthyl) failed to give [$2\text{-}C_{10}H_7CNi_3(\eta^5\text{-}C_5H_5)_3$]. The attempted synthesis of [$(\eta^5\text{-}C_5H_5)Ni(CH_2C{\equiv}CH)(PPh_3)$] from [$(\eta^5\text{-}C_5H_5)NiBr(PPh_3)$] and $CH{\equiv}CCH_2MgBr$ gave only [$(\eta^5\text{-}C_5H_5)Ni(C{\equiv}CMe)(PPh_3)$] by an unusual rearrangement reaction.

Introduction

The recent pioneering work of Seyferth and his coworkers [1] has illustrated that the stable alkylidynetricobalt nonacarbonyl cluster complexes, $RCCo_3(CO)_9$, not only have intriguing electronic properties [2] but are useful synthetic reagents. Our general interest [3—5] in the mechanisms of formation of these CCo_3 cluster complexes has lead us to investigate methods of synthesising related alkylidynetrimetal clusters. In 1972, it was reported by Voyevodskaya et al. [6] that the first methylidyne trinickel cluster compounds [$ArCNi_3(\eta^5\text{-}C_5H_5)_3$] (Ar = Ph or $p\text{-}MeC_6H_4$) had been accidently obtained from the reaction between nickelocene and $ArCH_2MgCl$. Since this report these compounds appear to have received no further attention, and to our knowledge no other examples of this type of compound have been described.

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* For Part I see ref. 18.

We now report the synthesis of the new compounds [$RCNi_3(\eta^5-C_5H_5)_3$] (R = CMe_3 and $SiMe_3$) by two different routes. Of particular interest is the isolation of these compounds from the reaction between the σ-alkyl derivatives [(η^5-C_5H_5)Ni(CH_2R)(PPh_3)] and nickelocene in the presence of n-BuLi. The mechanistic significance of this observation is discussed.

Results and discussion

Reaction between nickelocene and $PhCH_2MgBr$ in hexane at room temperature has been confirmed to yield [$PhCNi_3(\eta^5-C_5H_5)_3$] in 32% yield as an air-sensitive, black solid. Attempts to extend this reaction to the preparation of [n-$PrCNi_3$(η^5-C_5H_5)$_3$] by addition of n-BuLi to nickelocene (molar ratio 1/1) at room temperature resulted in complete decomposition of the nickelocene. Even when a 3/1 molar excess of nickelocene was employed cluster formation was not observed and approximately one mole of nickelocene decomposed. On the assumption that the decomposition may have been connected with the presence of β-hydrogens in the alkyl group, it was decided to repeat the reaction using alkyllithium reagents having no β-hydrogens. The reaction between nickelocene and methyllithium was unsuccessful and gave only a black, solid decomposition product. More success was achieved using the reagents RCH_2Li (R = Me_3C or Me_3Si) with a 3/1 molar excess of nickelocene for 1 h at room temperature. This gave the complexes [$Me_3CCNi_3(\eta^5-C_5H_5)_3$] and [$Me_3SiCNi_3(\eta^5-C_5H_5)_3$] in 22% and 15% yields, respectively. A repeat of the latter reaction using a 1/1 molar ratio at 40°C for 3 h gave a 12% yield of the compound [Me_3SiCNi_3(η^5-C_5H_5)$_2$(η^5-$C_5H_4CH_2SiMe_3$)] isolated as the only reaction product. The formation of this compound is in keeping with previous observations of Voyevodskaya et al. [6] that alkylation of a cyclopentadienyl ring of the initially formed cluster complex increases with increasing temperature and reaction time.

The trinickel cluster complexes have been fully characterised by elemental analysis, IR and ^{1}H NMR spectroscopy, and mass spectrometry. The NMR spectra of the compounds [$RCNi_3(\eta^3-C_5H_5)_3$] (R = CMe_3 or $SiMe_3$) show singlet peaks for the cyclopentadienyl ligands and the CH_3 groups in the expected intensity ratio of 15/9 (see Table 1). Their IR spectra show intense absorptions between 950—1150 cm^{-1} and 600—850 cm^{-1} characteristic of unsubstituted cyclopentadienyl ligands, and the compound where R = $SiMe_3$ has a strong ν(C—Si) absorption at 1237 cm^{-1}. In the mass spectra the natural abundances of the ^{58}Ni and ^{60}Ni isotopes (68% and 26.2%, respectively) enable the number of nickel atoms in each fragment to be determined accurately. Both compounds have a high intensity parent ion which breaks down with loss of either a $CCMe_3$ or $CSiMe_3$ fragment, and successive loss of cyclopentadienyl ligands. Characterisation of [$Me_3SiCNi_3(\eta^5-C_5H_5)_2(\eta^5-C_5H_4CH_2SiMe_3)$] is mainly on the basis of its mass spectrum, which shows a parent ion at m/e values of 540, 542, 544 and 546, and a breakdown pattern which follows closely those of the other two cluster compounds. The ^{1}H NMR spectrum shows two types of η^5=cyclopentadienyl ligand and both a Me_3Si and a Me_3SiCH_2 group (see Table 1).

A possible mechanistic scheme which accounts for the formation of these methylidyne trinickel clusters is outlined in Scheme 1. The first step is proposed

TABLE 1

^{1}H CHEMICAL SHIFTS [a, b]

Compound	
$PhCNi_3(\eta^5\text{-}C_5H_5)_3$	0.55 (m, 5, $C_6\underline{H}_5$); -1.4 (s, 15, $C_5\underline{H}_5$)
$Me_3CCNi_3(\eta^5\text{-}C_5H_5)_3$	-1.29 (s, 15, $C_5\underline{H}_5$); -4.92 (s, 9, $C\underline{H}_3$)
$Me_3SiCNi_3(\eta^5\text{-}C_5H_5)_3$	-1.47 (s, 15, $C_5\underline{H}_5$); -6.27 (s, 9, $C\underline{H}_3$)
$Me_3SiCNi_3(\eta^5\text{-}C_5H_5)_2(\eta^5\text{-}C_5H_4CH_2Me_3)$	-0.35 (s, 10, $C_5\underline{H}_5$); -0.53 (m, 4, $C_5\underline{H}_4$); -3.91 (m, 2, $C\underline{H}_2$); -6.13 (s, 9, $Si(C\underline{H}_3)_3$); -6.50 (s, 9, $CH_2Si(C\underline{H}_3)_3$)
$(\eta^5\text{-}C_5H_5)Ni(CH_2CMe_3)(PPh_3)$	0.74 (m, 15, $C_6\underline{H}_5$); -1.48 (s, 5, $C_5\underline{H}_5$); -5.93 (s, 9, $C\underline{H}_3$); -6.13 (d, 2, J(PH) 9 Hz, $C\underline{H}_2$)
$(\eta^5\text{-}C_5H_5)Ni(CH_2SiMe_3)(PPh_3)$	0.95 (m, 15, $C_6\underline{H}_5$); -1.53 (s, 5, $C_5\underline{H}_5$); -6.76 (s, 9, $C\underline{H}_3$); -7.98 (d, 2, J(PH) 10 Hz, $C\underline{H}_2$)
$(\eta^5\text{-}C_5H_5)Ni(CH_2C_{10}H_7\text{-}2)(PPh_3)$	0.89 (m, 22, $C_6\underline{H}_5$ and $C_{10}\underline{H}_7$); -1.82 (s, 5, $C_5\underline{H}_5$); -4.85 (d, 2, J(PH) 9 Hz, $C\underline{H}_2$)
$(\eta^5\text{-}C_5H_5)Ni(C{\equiv}CMe)(PPh_3)$	0.86 (m, 15, $C_6\underline{H}_5$); -1.53 (s, 5, $C_5\underline{H}_5$); -5.08 (d, 3, J(PH) 6 Hz, $C\underline{H}_3$)

[a] Saturated solutions in CS_2. All values quoted in ppm with reference to external benzene and positive values to high frequency (low field). [b] s singlet; d doublet; m complex multiplet.

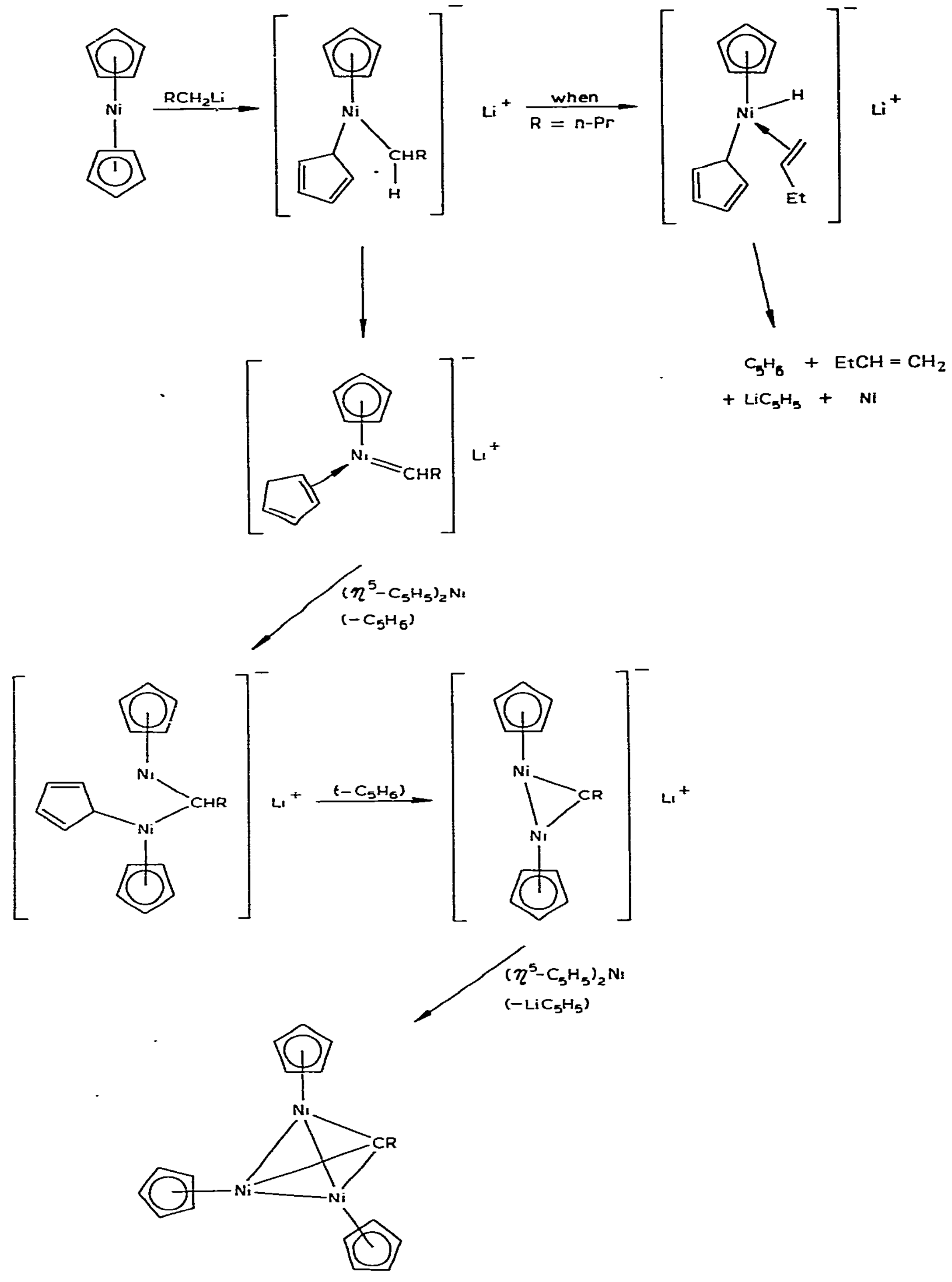
to be nucleophilic attack by the alkyllithium or Grignard reagent at the electron deficient [7] nickel atom of nickelocene with resulting σ—π rearrangement of one of the cyclopentadienyl ligands. In cases where the σ-alkyl ligand possesses a β-hydrogen this intermediate might be expected to be unstable, and would decompose via a β-hydride shift on to the nickel atom followed by reductive elimination of cyclopentadiene and the corresponding olefin. In cases where β-elimination is not possible, it is now well established [8] that α-hydrogen elimination can take place even under mild conditions to give a carbene intermediate, with, in this case, reductive elimination of cyclopentadiene. The proposed anionic carbene intermediate might be expected to have many of the properties of a carbanion, and react rapidly with more nickelocene to form an intermediate having a bridging carbyne ligand. This, on further reaction with nickelocene, could afford the trinickel cluster complexes.

Attempts to extend this reaction by carrying out the reaction of nickelocene with 2-naphthyllithium, 2- and 4-picolyllithium and prop-2-ynylmagnesium bromide failed to give any cluster compounds. It appears, therefore, that this method of synthesis is restricted to derivatives of benzyllithium or Grignard reagents and simple alkyllithium or Grignard reagents which do not possess β-hydrogens. Allylic Grignard reagents can not be employed as they yield stable η^3-allyl derivatives upon reaction with nickelocene [9].

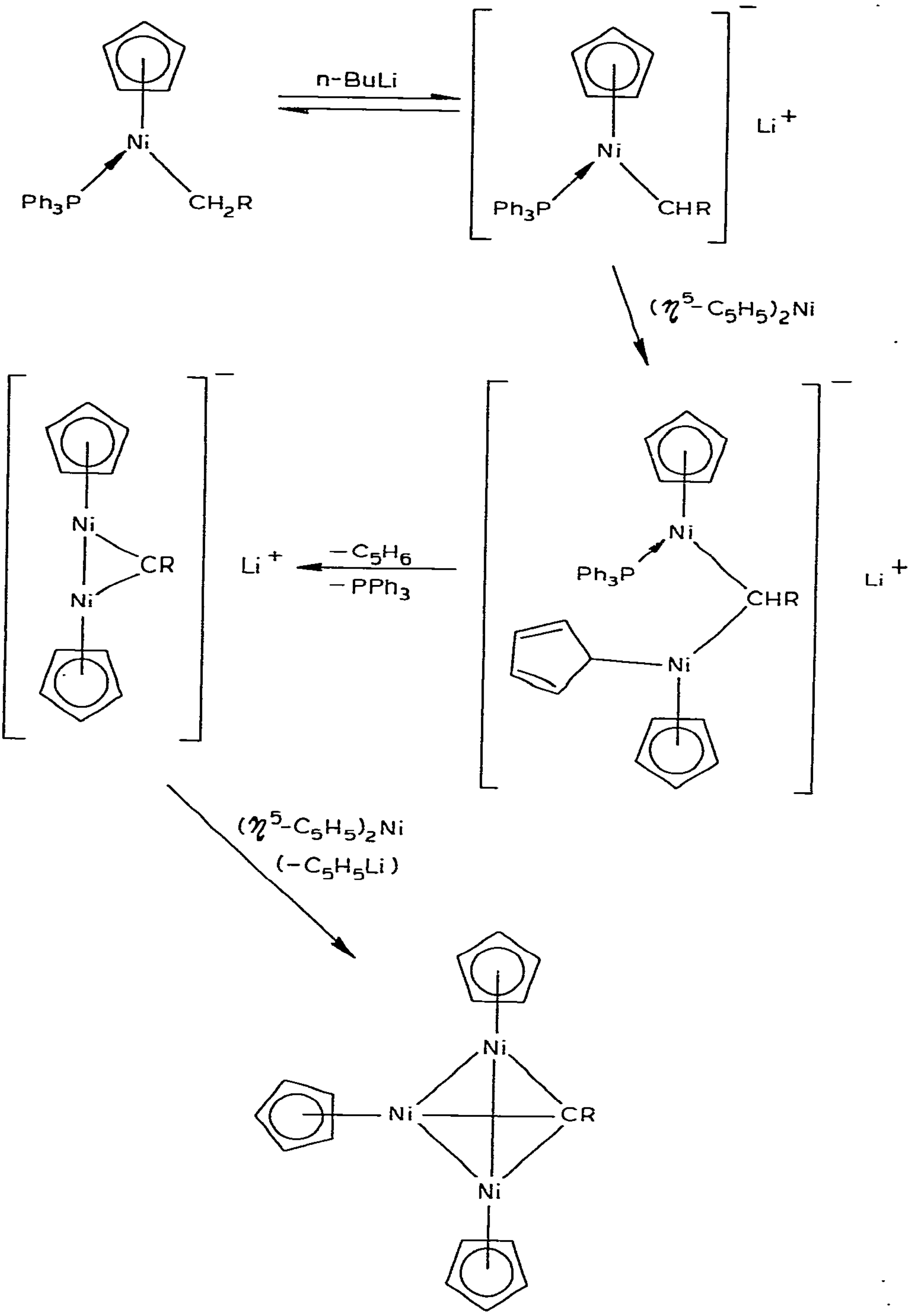
In an effort to find an alternative route to these cluster complexes the reactions of σ-alkylnickel compounds of the type $[(\eta^5\text{-}C_5H_5)Ni(CH_2R)(PPh_3)]$ were investigated. It was thought possible that, with a strong base, proton abstraction could lead to a carbanion intermediate $[(\eta^5\text{-}C_5H_5)Ni(CHR)(PPh_3)]^-$, which should have many of the properties of the intermediate $[(\chi^5\text{-}C_5H_5)Ni(\eta^2\text{-}C_5H_6)({=}CHR)]^-$ proposed in Scheme 1. Further reaction of the carbanion intermediate could give cluster formation as shown in Scheme 2.

(Continued on p. 376)

SCHEME 1


Ni
RCH_2Li
Ni
CHR
H
Li⁺
when
R = n-Pr
Ni
H
Et
Li⁺
C_5H_6 + $EtCH=CH_2$
+ LiC_5H_5 + Ni
Ni
CHR
Li⁺
$(\eta^5\text{-}C_5H_5)_2Ni$
$(-C_5H_6)$
Ni
CHR
Ni
Li⁺
$(-C_5H_6)$
Ni
CR
Ni
Li⁺
$(\eta^5\text{-}C_5H_5)_2Ni$
$(-LiC_5H_5)$
Ni
CR
Ni
Ni

SCHEME 2


Ni
Ph$_3$P
CH$_2$R
n-BuLi
Ni
Ph$_3$P
CHR
Li$^+$
$(\eta^5\text{-}C_5H_5)_2Ni$
Ni
Ph$_3$P
CHR
Ni
Li$^+$
$-C_5H_6$
$-PPh_3$
Ni
CR
Ni
Li$^+$
$(\eta^5\text{-}C_5H_5)_2Ni$
$(-C_5H_5Li)$
Ni
Ni
CR
Ni

The known compounds [(η^5-C_5H_5)Ni(CH_2R)(PPh_3)] (R = Me, Et or n-Pr) were avoided as they are reported to be only moderately stable in solution, and readily undergo β-hydrogen elimination on heating [10,11]. The previously unreported derivatives where R = Me_3C, Me_3Si and 2-$C_{10}H_7$ were prepared in 43–55% yield by the standard reaction of [(η^5-C_5H_5)NiBr(PPh_3)] with the corresponding organolithium reagent in benzene at 0°C. The green, air sensitive solids were fully characterised by elemental analysis, IR and ^1H NMR spectroscopy The ^1H NMR spectra (see Table 1) all show a characteristic band to high field of the external benzene reference for the σ-CH_2 group, which appears as a doublet due to coupling with the ^{31}P nucleus of the phosphine ligand. The exceptionally high chemical shift observed for the methylene protons of the Me_3SiCH_2 group reflects the powerful shielding effect of the Me_3Si moiety as noted previously by other workers [12,13].

When an equimolar amount of n-BuLi was added to benzene solutions of [(η^5-C_5H_5)Ni(CH_2R)(PPh_3)] (R = Me_3C, Me_3Si or Ph) containing an excess of nickelocene at room temperature, an immediate reaction occurred and, upon work-up of the reaction mixture, the corresponding alkylidyne trinickel cluster complexes were isolated in 7–9% yield. No evidence for cluster formation was obtained in the reaction of [(η^5-C_5H_5)Ni($CH_2C_{10}H_7$-2)(PPh_3)] under similar conditions, and it does appear that the cluster [2-$C_{10}H_7CNi_3$(η^5-C_5H_5)$_3$] is particularly unstable, possibly for steric reasons.

Reaction between [(η^5-C_5H_5)NiBr(PPh_3)] and 2- and 4-picolyllithium failed to give the corresponding σ-alkylnickel derivatives. The reason for this is not clear. There seems no obvious reason why these complexes should be unstable unless the alkyllithium reagents do not behave as carbanionic nucleophiles, but exhibit ambident behaviour. In this case attack at nickel could occur via the ring nitrogen atom and could well lead to an unstable intermediate. This failure to form σ-alkylnickel complexes using these particular reagents would, on the basis of Scheme 1, explain the earlier failure to obtain clusters from the same reagents.

The reaction between prop-2-ynylmagnesium bromide and [(η^5-C_5H_5)NiBr(PPh_3)] (1/1 molar ratio) in benzene at 0°C was also unusual in that the reaction product proved to be the prop-1-ynyl derivative [(η^5-C_5H_5)Ni(C≡CMe)(PPh_3)], isolated in 36% yield. This compound has recently been obtained from the reaction between [$(HNEt_2)_n$CuC≡CMe] and [(η^5-C_5H_5Ni(PPh_3)Br], but no physical or spectroscopic data were given [14]. Its IR spectrum showed a characteristic band at 2115 cm^{-1} [ν(C≡C)], but no bands in the region of 3310–3320 cm^{-1} anticipated for the stretching vibration of an acetylenic hydrogen. The ^1H NMR spectrum (Table 1) shows, in addition to bands at −1.53 and 0.86 ppm (with reference to external benzene) for the C_5H_5 and PPh_3 ligands respectively, only one other band, a doublet at −5.09 ppm. The chemical shift of this band is very different from that expected for a σ-prop-2-ynyl metal derivative which all show a characteristic band at ca. τ 9 (i.e., ca. −6.27 ppm relative to external benzene) and a band at ca. τ 8 (−5.27 ppm relative to external benzene) in the intensity ratio of 2/1 [15]. The simplicity of the spectrum rules out the alternative σ-allenyl structure.

It is not clear how this product arises. An NMR spectrum of a sample isolated directly from the reaction mixture has established that rearrangement does not occur during the work-up procedure. There is some chemical evidence that the Grignard reagent prepared from $CH{\equiv}CCH_2Br$ by the standard literature method [16] may be a mixture of $CH{\equiv}CCH_2MgBr$ and $CH_2{=}C{=}CHMgBr$. It is reported to yield the expected products, $CH{\equiv}CCH_2C(OH)RR'$, upon reaction with ketones, RCOR′, but on hydrolysis a mixture of $MeC{\equiv}CH$ and $CH_2{=}C{=}CH_2$ is obtained, and carbonation, even at −80°C gives both $CH{\equiv}CCH_2CO_2H$ and $CH_2{=}C{=}CHCO_2H$ [17]. It is also reported that on heating above 20°C the Grignard reagent rearranges to $MeC{\equiv}CMgBr$ and $BrMgC{\equiv}CCH_2MgBr$ over a period of ca. 5 h. As the reaction with $[(\eta^5\text{-}C_5H_5)NiBr(PPh_3)]$ was carried out at 0°C for only 0.5 h it is unlikely that this rearrangement could account for the formation of the prop-1-ynyl complex. Similarly, it is difficult to appreciate how the observed product could be formed by rearrangement of the two possible intermediates $[(\eta^5\text{-}C_5H_5)Ni(CH_2C{\equiv}CH)(PPh_3)]$ and $[(\eta^5\text{-}C_5H_5)Ni(CH{=}C{=}CH_2)(PPh_3)]$. The absence of a β-hydrogen rules out reversible 1,2-hydrogen transfer via the metal atom, and the geometries of both the σ-prop-2-ynyl and σ-allenyl ligands appear to exclude an intramolecular 1,3-hydrogen shift. It is apparent, however, that if formation of a prop-1-ynyl complex is a general feature of reactions of $CH{\equiv}CCH_2MgBr$ with transition metal compounds it would explain why a trinickel cluster complex was not obtained from the reaction with nickelocene.

Experimental

IR spectra were recorded as Nujol and HCB mulls on a Perkin—Elmer 621 spectrophotometer. ^1H NMR spectra were determined on CS_2 solutions with benzene as external reference on a Perkin—Elmer R10 instrument, and mass spectra were obtained using an A.E.I. MS902 mass spectrometer operating at an ionising energy of 70 eV. All solvents were thoroughly dried by standard procedures and distilled before use. Except where stated all reactions were carried out under dry argon, and all manipulations, including chromatography, were done under dry nitrogen.

Reactions of nickelocene

(a) With 2,2-dimethylpropyllithium. A solution of Me_3CCH_2Li (0.19 g, 2.50 mmol) in hexane (6 ml) was added dropwise to a solution of nickelocene (1.40 g, 7.41 mmol) in hexane (60 ml) at 0°C. After stirring the mixture for 2 h at this temperature it was filtered to remove a light brown solid (0.91 g), and the green filtrate was chromatographed on alumina (grade III) with hexane as eluent to give nickelocene (51 mg, 0.27 mmol, 4% recovery), and $[Me_3CCNi_3(\eta^5\text{-}C_5H_5)_3]$ (0.24 g, 0.54 mmol, 22%) as a black solid, m.p. 191—196°C (dec.). Anal.: Found: C, 54.7; H, 5.7. $C_{20}H_{24}Ni_3$ calcd.: C, 54.4; H, 5.4%. Purified by sublimation at 115—120°C/1 mmHg.

A repeat of this procedure using nickelocene (1.12 g, 5.93 mmol) and an excess of Me_3CCH_2Li (0.65 g, 8.31 mmol) gave $[Me_3CCNi_3(\eta^5\text{-}C_5H_5)_3]$ (0.65 g, 8.31 mmol).

(b) With trimethylsilylmethyllithium. Dropwise addition of Me_3SiCH_2Li (0.15 g, 1.62 mmol) in hexane (5.5 ml) to a hexane solution of nickelocene (0.90 g, 4.76 mmol) at room temperature gave a dark brown solution. After stirring for 1 h the solution was filtered to remove a light brown solid (0.28 g), and

chromatography (grade II, alumina) using hexane as eluent gave recovered nickelocene (50 mg), and [$Me_3SiCNi_3(\eta^5$-$C_5H_5)_3$] as a black-violet solid (0.21 g, 0.41 mmol, 15%), m.p. 195—202°C (dec.). Anal.: Found: C, 50.2; H, 5.6. $C_{19}H_{24}Ni_3Si$ calcd.: C, 49.9; H, 5.3%. Purified by sublimation at 80—90°C/1 mmHg.

When this reaction was repeated using an excess of Me_3SiCH_2Li (0.51 g, 5.40 mmol) over nickelocene (0.97 g, 5.10 mmol) and the hexane solution was stirred at 40°C for 3 h, chromatography gave [$Me_3SiCNi_3(\eta^5$-$C_5H_5)_2(\eta^5$-$C_5H_4CH_2SiMe_3)$] (0.10 g, 0.20 mmol, 12%), as a dark brown solid, m.p. 204—206°C (dec.). Anal.: Found: C, 50.4; H, 5.9. $C_{23}H_{34}Ni_3Si_2$ calcd.: C, 50.8; H, 6.2%. Purified by sublimation at 100—110°C/1 mmHg.

Reactions of [(η^5-C_5H_5)NiBr(PPh_3)] (17)

(a) With 2,2-dimethylpropyllithium. A solution of Me_3CCH_2Li (0.46 g, 5.95 mmol) in hexane (17 ml) was added dropwise over a period of 20 min to a solution of [(η^5-C_5H_5)NiBr(PPh_3)] (2.60 g, 5.60 mmol) in benzene (40 ml) at 0°C, and the mixture was stirred at room temperature for 1 h. Chromatography (alumina, grade I) using a 1/1 hexane/benzene mixture as eluent gave [(η^5-C_5H_5)-Ni(CH_2CMe_3)(PPh_3)] (1.41 g, 3.08 mmol, 55%) as dark green crystals, m.p. 111—113°C (dec.). Anal.: Found: C, 73.7; H, 7.1. $C_{28}H_{31}NiP$ calcd.: C, 73.5; H, 6.8%. Purified by recrystallisation from a benzene/n-pentane mixture at —10°C.

(b) With trimethylsilylmethyllithium. Following the same procedure as outlined above reaction between Me_3SiCH_2Li (0.45 g, 4.8 mmol) and [(η^5-C_5H_5)-NiBr(PPh_3)] (2.22 g, 4.76 mmol) gave dark green crystals of [(η^5-C_5H_5)Ni(CH_2-$SiMe_3$)(PPh_3)] (1.22 g, 2.58 mmol, 54%), m.p. 118—120°C (dec.). Anal.: Found: C, 68.6; H, 6.5. $C_{27}H_{31}NiPSi$ calcd.: C, 68.5; H, 6.6%.

(c) With 2-naphthylmethyllithium. Dropwise addition of 2-naphthylmethyllithium (1.04 g, 7.0 mmol) in THF (14 ml) to a solution of [(η^5-C_5H_5)NiBr-(PPh_3)] (3.15 g, 6.76 mmol) in benzene (60 ml) at 0°C, gave, after stirring for 0.5 h, brown-yellow crystals of [(η^5-C_5H_5)Ni($CH_2C_{10}H_7$-2)(PPh_3)] (1.53 g, 2.90 mmol, 43%), m.p. 192—195°C (dec.). Anal. Found: C, 77.4; H, 6.2. $C_{34}H_{29}NiP$ calcd.: C, 77.4; H, 5.5%). Recrystallised from a benzene/pentane mixture at —10°C.

(d) With prop-2-ynylmagnesium bromide. A solution of prop-2-ynyl magnesium bromide (0.86 g, 6.00 mmol) in THF (4 ml) was added to a solution of [(η^5-C_5H_5)NiBr(PPh_3)] (2.22 g, 4.76 mmol) in benzene (50 ml) at 0°C, and after stirring at this temperature for 0.5 h, the mixture was chromatographed (alumina, grade I, 1/1 benzene/hexane eluent) to give [(η^5-C_5H_5)Ni($C{\equiv}CMe$)-(PPh_3)] (0.73 g, 1.72 mmol, 36%), as dark green crystals, m.p. 105—109°C (dec.). Anal.: Found: C, 73.0; H, 5.6%. $C_{26}H_{23}NiP$ calcd.: C, 73.4; H, 5.4%.

Reaction of [(η^5-C_5H_5)Ni(CH_2Ph)(PPh_3)] with nickelocene

A solution of n-butyllithium (0.15 g, 2.40 mmol) in ether (6 ml) was added to a solution of [(η^5-C_5H_5)Ni(CH_2Ph)(PPh_3)] [11] and nickelocene (1.34 g, 7.10 mmol) in benzene (50 ml) at room temperature, and the mixture was stirred for 1 h. Chromatography (alumina, grade III; hexane eluent) gave recovered nickelocene (45 mg), and [$PhCNi_3(\eta^5$-$C_5H_5)_3$] (92 mg, 0.20 mmol, 9%) as a black solid, m.p. 158—160°C (lit. [6] m.p. 158—160°C) identified by comparison of its IR and ^1H NMR spectra with those of an authentic sample prepared by reaction of nickelocene with $PhCH_2MgBr$.

Reaction of $[(\eta^5\text{-}C_5H_5)Ni(CH_2CMe_3)(PPh_3)]$ *with nickelocene*

Addition of n-butyllithium (0.20 g, 3.20 mmol) to a solution of $[(\eta^5\text{-}C_5H_5)\text{-}Ni(CH_2CMe_3)(PPh_3)]$ (1.41 g, 3.08 mmol) and nickelocene (2.68 g, 14.2 mmol) in benzene following the procedure described above, gave recovered nickelocene (53 mg), and $[Me_3CCNi_3(\eta^5\text{-}C_5H_5)_3]$ (0.12 g, 0.27 mmol, 9%).

Reaction of $[(\eta^5\text{-}C_5H_5)Ni(CH_2SiMe_3)(PPh_3)]$ *with nickelocene*

Reaction between n-butyllithium (0.22 g, 3.40 mmol) and a solution of $[(\eta^5\text{-}C_5H_5)Ni(CH_2SiMe_3)(PPh_3)]$ (1.52 g, 3.22 mmol) and nickelocene (2.51 g, 13.3 mmol) in benzene at room temperature for 1 h, gave, after chromatography, recovered nickelocene (0.84 g, 4.45 mmol, 32%), and $[Me_3SiCNi_3(\eta^5\text{-}C_5H_5)_3]$ (0.11 g, 0.24 mmol, 7%).

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