Synthesis and Reactions of Nickel(0) η^2-Cyclohexyne Complexes and X-ray Crystal Structure of $Ni(\eta^2\text{-}C_6H_8)((C_6H_{11})_2PCH_2CH_2P(C_6H_{11})_2)$

Martin A. Bennett,* Julian A. Johnson, and Anthony C. Willis

Research School of Chemistry, The Australian National University, Canberra, ACT 0200, Australia

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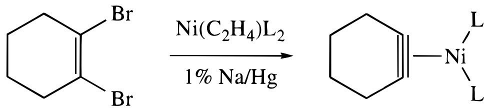
Reduction of 1,2-dibromocyclohexene with 1% sodium amalgam in the presence of $Ni(\eta^2\text{-}C_2H_4)L_2$ gives cyclohexyne nickel(0) complexes $Ni(\eta^2\text{-}C_6H_8)L_2$ [$L_2 = 2PPh_3$ (**1**), dcpe (**2**), $2PEt_3$ (**3**); dcpe = 1,2-bis(dicyclohexylphosphino)ethane, $Cy_2PCH_2CH_2PCy_2$], which are structurally similar to, but less stable than, the corresponding platinum(0) compounds. The crystal structure of **2** has been determined. The molecule contains a nickel atom bound to η^2-cyclohexyne [Ni−C(1) = 1.875(4) Å, Ni−C(2) = 1.867(4) Å] and to dcpe [Ni−P(1) = 2.139(1) Å, Ni−P(2) = 2.138(1) Å]. The geometry is close to trigonal planar if the midpoint of the coordinated triple bond is regarded as occupying one coordination site, and the C═C distance [1.272(5) Å] is slightly less than that in $Pt(\eta^2\text{-}C_6H_8)(PPh_3)_2$ [1.297(8) Å]. Complex **2** reacts with methyl iodide and with CO_2 to give insertion products containing nickel(II), $NiI(2\text{-}MeC_6H_8)$(dcpe) (**7**) and $Ni\{C_6H_8C(O)O\}$(dcpe)(**9**), respectively. Dimethyl acetylenedicarboxylate inserts into the Ni−C σ-bond of **9** to give a seven-membered nickelacycle $Ni\{C(CO_2Me){=}C(CO_2Me)C_6H_8C(O)O\}$(dcpe) (**10**).

Introduction

Small cyclic alkynes such as cycloheptyne (C_7H_{10}) and cyclohexyne (C_6H_8) exist only transiently in the free state, but can be stabilized in the form of transition metal complexes of platinum(0), palladium(0), and zirconium(II), such as $M(\eta^2\text{-}C_7H_{10})L_2$ (M = Pt, Pd; L_2 = $2PPh_3$, dppe),[1−4] $M(\eta^2\text{-}C_6H_8)L_2$ (M = Pt, $L_2 = 2PPh_3$,[2−4] $2P\text{-}t\text{-}BuPh_2$,[5] $2P\text{-}t\text{-}Bu_2Ph$,[5] $2PMe_3$,[5] dppe,[2,4] dppp,[6] dmpe;[5] M = Pd, $L_2 = 2PPh_3$, dppe[4]), and $Zr(\eta^5\text{-}C_5H_5)_2(\eta^2\text{-}C_6H_8)(PMe_3)$.[7] Because complexes of nickel(0) are usually structurally similar to their palladium(0) and platinum(0) counterparts, but are often more air-sensitive and catalytically more active,[8,9] we were interested to determine whether cycloalkyne complexes of nickel(0) corresponding to the palladium(0) and platinum(0) complexes and to the η^2-benzyne nickel(0) complexes $Ni(\eta^2\text{-}C_6H_4)L_2$ (2L = $2PEt_3$, dcpe)[10,11] could be made. The results of the investigation are described in this paper.

Results

The cyclohexyne nickel(0) complexes $Ni(\eta^2\text{-}C_6H_8)L_2$ [$L_2 = 2PPh_3$ (**1**), dcpe (**2**)] can be isolated as yellow, air-sensitive solids in *ca.* 60% yield from the reduction of 1,2-dibromocyclohexene with 1% sodium amalgam in the presence of $Ni(\eta^2\text{-}C_2H_4)L_2$ (eq 1); this procedure is similar to that used for the preparation of $Pt(\eta^2\text{-}C_6H_8)(PPh_3)_2$.[2,4]



(1)

2L = $2PPh_3$ (**1**), dcpe (**2**), $2PEt_3$ (**3**)

The triethylphosphine complex $Ni(\eta^2\text{-}C_6H_8)(PEt_3)_2$ (**3**) was isolated similarly as a yellow oil that could not be crystallized, even from pentane at −78 °C. The IR spectrum of **1** shows a strong band at 1735 cm^{-1}, which is assigned to $\nu(C{\equiv}C)$ modified by coordination. It is *ca.* 14 cm^{-1} higher frequency than the corresponding absorption in $Pt(\eta^2\text{-}C_6H_8)(PPh_3)_2$,[2,4] in accord with the trend observed for Ni(0) and Pt(0) complexes of acyclic acetylenes.[12,13] The $\nu(C{\equiv}C)$ bands in the spectra of **2** and **3** are *ca.* 20 cm^{-1} lower frequency than those in **1**, probably due to increased back-bonding into the cyclohexyne π^*-orbitals induced by the more electron-donating alkylphosphines.[6,13,14] The $^{31}P\{^1H\}$ NMR spectra of

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(1) Abbreviations: dppe, 1,2-bis(diphenylphosphino)ethane, $Ph_2PCH_2CH_2PPh_2$; dppp, 1,3-bis(diphenylphosphino)propane, $Ph_2PCH_2CH_2CH_2PPh_2$; dppb, 1,4-bis(diphenylphosphino)butane, $Ph_2PCH_2CH_2CH_2CH_2PPh_2$; dmpe, 1,2-bis(dimethylphosphino)ethane, $Me_2PCH_2CH_2PMe_2$; dcpe, 1,2-bis(dicyclohexylphosphino)ethane, $Cy_2PCH_2CH_2PCy_2$.

(2) Bennett, M. A.; Robertson, G. B.; Whimp, P. O.; Yoshida, T. *J. Am. Chem. Soc.* **1971**, *93*, 3797.

(3) Robertson, G. B.; Whimp, P. O. *J. Am. Chem. Soc.* **1975**, *97*, 1051.

(4) Bennett, M. A.; Yoshida, T. *J. Am. Chem. Soc.* **1978**, *100*, 1750.

(5) Bennett, M. A.; Fick, H.-G.; Warnock, G. F. *Aust. J. Chem.* **1992**, *45*, 135.

(6) Bennett, M. A.; Rokicki, A. *Aust. J. Chem.* **1985**, *38*, 1307.

(7) Buchwald, S. L.; Lum, R. T.; Dewan, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 7441.

(8) Jolly, P. W.; Wilke, G. *The Organic Chemistry of Nickel;* Academic: New York and London, 1974; Vol. 1 (1975, Vol. 2).

(9) Jolly, P. W. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 6, pp 1−231; Vol. 8, pp 613−797.

(10) Bennett, M. A.; Hambley, T. W.; Roberts, N. K.; Robertson, G. B. *Organometallics* **1985**, *4*, 1992.

(11) Bennett, M. A.; Wenger, E. *Organometallics* **1995**, *14*, 1267.

(12) Greaves, E. O.; Lock, C. J. L.; Maitlis, P. M. *Can. J. Chem.* **1968**, *46*, 3879.

(13) Rosenthal, U. *Z. Anorg. Allgem. Chem.* **1981**, *482*, 179.

(14) Rosenthal, U.; Schulz, W. *J. Organomet. Chem.* **1987**, *321*, 103.

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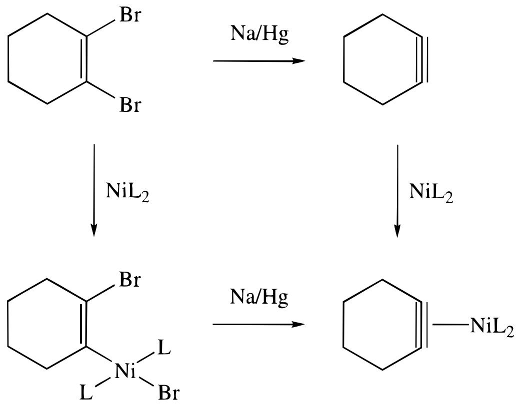
1−**3** each show a singlet and in the ^{13}C NMR spectra there is a characteristic five-line AA′X pattern at δ *ca.* 140 due to the coordinated carbon atoms, the separation of the outer lines, $J(PC) + J(P'C)$, being *ca.* 80 Hz. Similar patterns have been observed in the ^{13}C NMR spectra of benzyne nickel(0) complexes,[10,11] cycloalkyne platinum(0) complexes,[5] and alkyne complexes $M(\eta^2\text{-}RC_2R)(PR'_3)_2$ (M = Ni, Pt);[15,16] they confirm that rotation of the coordinated cyclohexyne is slow on the NMR time scale. The EI mass spectrum of **2** shows a parent ion at *m*/*z* 560, but parent ions were not observed for **1** and **3**. The analytical and spectroscopic data thus strongly support the formulation as cyclohexyne nickel(0) complexes, and this has been confirmed in the case of **2** by X-ray structural analysis (see the following).

Complexes **1** and **3** were also formed from 1,2-dibromocyclohexene and 1% Na/Hg in the presence of $Ni(COD)_2$ and 2 equiv of PPh_3 or PEt_3, but in the case of PPh_3 some $Ni(PPh_3)_3$ was also formed, as shown by ^{31}P NMR spectroscopy.[17,18] A similar reaction with PMe_3 (2 equiv), dppe (1 equiv), or depe (1 equiv) gave, respectively, $Ni(PMe_3)_4$,[19] $Ni(dppe)_2$,[20] and $Ni(depe)_2$[21] as the only products identifiable by ^{31}P NMR spectroscopy. Under the same conditions, dmpe (1 equiv) afforded an oil, which was shown by ^{31}P NMR spectroscopy to contain two products in *ca.* 3:1 ratio. The main product was $Ni(dmpe)_2$ (δ_P 18.0);[19,22] the minor product (δ_P 24.5) may be $Ni(\eta^2\text{-}C_6H_8)(dmpe)$, because the IR spectrum of the oil contained a weak band at 1715 cm^{-1} assignable to $\nu(C{\equiv}C)$ modified by coordination. The two species could not, however, be separated by fractional crystallization.

Reduction of 1,2-dibromocyclohexene with 1% Na/Hg in the presence of $Ni(\eta^2\text{-}C_2H_4)(PCy_3)_2$ gave, after 24 h, an oil whose IR spectrum showed a band of medium intensity at 1720 cm^{-1}, indicative of the presence of $Ni(\eta^2\text{-}C_6H_8)(PCy_3)_2$ (**4**). The $^{31}P\{^1H\}$ NMR spectrum of the oil showed four main singlets at δ 9, 37, 45, and 49, the first two being due to unchanged PCy_3 and $Ni(\eta^2\text{-}C_2H_4)(PCy_3)_2$, respectively, and the third due to $Ni(PCy_3)_3$.[23] After 36 h the peak at δ 49, presumed to be due to **4**, had disappeared, and only those due to PCy_3 and $Ni(PCy_3)_3$ remained.

Attempts to prepare nickel(0) cyclohexyne complexes containing ditertiary phosphines by displacement of PPh_3 from **1** were only partly successful, in contrast to the behavior of the corresponding platinum(0) system.[6] The IR spectrum of the yellow solid isolated from the reaction of **1** with dppe in benzene at room temperature showed a strong band at 1720 cm^{-1} due to $Ni(\eta^2\text{-}C_6H_8)(dppe)$ (**5**), but the ^{31}P NMR spectrum showed the presence of $Ni(dppe)_2$ (δ_P 43.0) (*ca.* 20%) in addition to **5** (δ_P 60.2). Under similar conditions, reaction of **1** with dcpe gave an approximately 1:1 mixture of **2** and $Ni(dcpe)_2$ (δ_P 43.5).[24]

Scheme 1. Possible Routes to Cyclohexyne Nickel(0) Complexes



In the complete absence of air, solutions of **1**−**3** in benzene are stable for 2 weeks before appreciable decomposition occurs. In the case of **1**, formation of a black deposit is accompanied in the $^{31}P\{^1H\}$ NMR spectrum by the growth of a singlet at δ 24.0, probably due to $Ni(PPh_3)_3$, as well as other broad, ill-defined peaks. Complex **2** slowly gives two species characterized by ^{31}P NMR singlets at δ 55 and 60 that have not been investigated further.

The reaction described by eq 1 could proceed by two routes, as summarized in Scheme 1. First, cyclohexyne, generated transiently from 1,2-dibromocyclohexene and 1% Na/Hg,[27−29] could react with the zero-valent metal complex. This idea was behind the original synthesis of $Pt(\eta^2\text{-}C_6H_8)(PPh_3)_2$[2,4] and has also been suggested for the corresponding formation of the 4-homoadamantyne complex $Pt(\eta^2\text{-}C_{11}H_{14})(PPh_3)_2$ from 4,5-dibromo-4-homoadamantene.[30] In the second possible pathway, 1,2-dibromocyclohexene could undergo oxidative addition to the nickel(0) complex to give a (2-bromocyclohexenyl)nickel(II) bromide, $NiBr(2\text{-}BrC_6H_8)L_2$, which could be reduced to $Ni(\eta^2\text{-}C_6H_8)L_2$ by 1% Na/Hg. The synthesis of the closely related benzyne complex $Ni(\eta^2\text{-}C_6H_4)(dcpe)$ by alkali metal reduction of $NiBr(2\text{-}BrC_6H_4)(dcpe)$[10] provides a close analogy. In contrast, (2-bromocycloalkenyl)platinum(II) complexes $PtBr(C_nH_{2n-4}Br)L_2$ ($n = 5$, 6) are not reduced by 1% Na/Hg to the corresponding cycloalkyne platinum(0) complexes. In the case of $n = 5$, however, it has been shown that the cyclopentyne complex $Pt(\eta^2\text{-}C_5H_6)(PPh_3)_2$ is formed by 1% Na/Hg reduction of the π-complex of 1,2-dibromocyclopentene,

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[15] Pörschke, K. R.; Mynott, R.; Angermund, K.; Krüger, C. *Z. Naturforsch. B* **1985**, *40*, 199.

[16] Boag, N. M.; Green, M.; Grove, D. M.; Howard, J. A. K.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1980**, 2170.

[17] Tolman, C. A.; Seidel, W. C.; Gerlach, D. H. *J. Am. Chem. Soc.* **1972**, *94*, 2669.

[18] Mynott, R.; Mollbach, A.; Wilke, G. *J. Organomet. Chem.* **1980**, *199*, 107.

[19] Tolman, C. A.; Seidel, W. C.; Gosser, L. W. *J. Am. Chem. Soc.* **1974**, *96*, 53.

[20] Fisher, K. J.; Alyea, E. C. *Polyhedron* **1989**, *8*, 13.

[21] A sample of $Ni(depe)_2$ prepared *in situ* by the addition of depe (2 equiv) to $Ni(COD)_2$ in C_6D_6 showed a $^{31}P\{^1H\}$ NMR singlet at δ_P 44.7.

[22] Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2956.

[23] Jolly, P. W.; Jonas, K.; Krüger, C.; Tsay, Y.-H. *J. Organomet. Chem.* **1971**, *33*, 109.

[24] This compound has been made as bright yellow crystals by the reduction of $Ni(acac)_2$ with Et_2AlOEt in toluene/ether in the presence of dcpe (2 equiv).[25] It is clearly different from the purple product isolated from the reaction of nickelocene with dcpe in refluxing toluene, which has been formulated as a three-coordinate species, Ni(dcpe-PP′)(dcpe-P).[26]

[25] Büch, H. M. Ph.D. Thesis, University of Kaiserslautern, 1982, p 210.

[26] Connor, J. A.; Riley, P. I. *Inorg. Chim. Acta* **1968**, *15*, 217.

[27] Favorsky, A.; Bushowsky, M. *Justus Liebigs Ann. Chem.* **1912**, *390*, 122.

[28] Wittig, G.; Mayer, U. *Chem. Ber.* **1963**, *96*, 329, 342. (b) Wittig, G.; Weinlich, J. *Chem. Ber.* **1965**, *98*, 471.

[29] (a) Wittig, G.; Krebs, A. *Chem. Ber.* **1961**, *94*, 3260. (b) Wittig, G.; Pohlke, R. *Chem. Ber.* **1961**, *94*, 3276.

[30] Komatsu, K.; Kamo, H.; Tsuji, R.; Masuda, H.; Takeuchi, K. *J. Chem. Soc., Chem. Commun.* **1991**, 71.

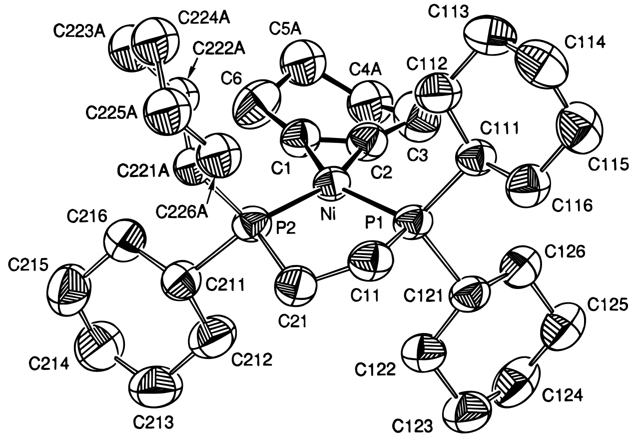

Figure 1. Molecular structure of $Ni(\eta^2-C_6H_8)(Cy_2PCH_2CH_2PCy_2)$ (**2**) with atom labeling and 50% probability ellipsoids.

$Pt(\eta^2-C_5H_6Br_2)(PPh_3)_2$.[31] Moreover, the formation of the cycloheptyne complex $Pt(\eta^2-C_7H_{10})(PPh_3)_2$ from 1-bromocycloheptene, LiN-i-Pr_2, and $Pt(PPh_3)_3$ appears to proceed by elimination of HBr from an intermediate π-complex $Pt(\eta^2-C_7H_{11}Br)(PPh_3)_2$, rather than via free cycloheptyne.[32]

In an attempt to find out which pathway is operative in the reaction described by eq 1, we studied the reaction of an excess of 1,2-dibromocyclohexene with $Ni(\eta-C_2H_4)$(dcpe) in the absence of 1% Na/Hg. The main product, formed over the course of 24 h, was $NiBr_2$(dcpe), as shown by ^{31}P NMR spectroscopy, but a small amount of a product having an AB quartet (δ_P 61.4, 64.9; J_{AB} = 11.4 Hz) was also present; it may be $NiBr(2-BrC_6H_8)$(dcpe) (**6**). The second product was formed in a much higher proportion by the addition of 1,2-dibromocyclohexene to **2**, but attempts to isolate it in a pure state failed, and over 48 h it decomposed to $NiBr_2$(dcpe). Reduction of impure **6** with 1% Na/Hg gave **2** as the main product, identified *in situ* by comparison of its $^{31}P\{^1H\}$ NMR and IR spectra with those of an authentic sample. These results indicate that **6** is a plausible intermediate in the synthesis of **2**, but do not rule out the possible involvement of free cyclohexyne.

Structure of $Ni(\eta^2-C_6H_8)$(dcpe) (2). The molecular structure with atom labeling is shown in Figure 1; selected bond lengths and bond angles are summarized in Table 1, and details of the data collection are given in Table 2. The molecule consists of a central nickel atom symmetrically coordinated by η^2-cyclohexyne [r(Ni−C1) 1.875(4) Å, r(Ni−C2) = 1.867(4) Å] and the ditertiary phosphine [r(Ni−P1) = 2.139(1) Å, r(Ni−P2) = 2.138(1) Å] in an arrangement that is close to trigonal planar, on the assumption that the midpoint of the coordinated triple bond occupies one coordination site. This coordination geometry is typical of $M(\eta^2$-alkyne)L_2 complexes of the d^{10} metals.[33] The dihedral angle between the Ni−P1−P2 and Ni−C1−C2 planes is 3.8°. The M−C and M−P distances in **2** are *ca.* 0.15 Å shorter than those in $Pt(\eta^2-C_6H_8)(PPh_3)_2$,[3] but are similar to those in $Ni(\eta^2-C_6H_4)$(dcpe) [Ni−P 2.203(4) Å, 2.170(4) Å; Ni−C 1.951(12) Å, 1.988(12) Å].[10] The Ni−C and Ni−P distances in **2** are also comparable with those observed in bis(tertiary phosphine)nickel(0) complexes of acyclic alkynes, $Ni(RC_2R)L_2$ (2L = $2PPh_3$,[34] R = H, $SiMe_3$,[35] CO_2Me;[36] 2L = dmpe, R = Ph[15]). The C1−C2 bond distance of 1.272(5) Å in **2** falls within the range 1.25−1.30 Å found in $Ni(\eta^2-RC_2R)L_2$ complexes and is slightly less than that in $Pt(\eta^2-C_6H_8)(PPh_3)_2$ [1.297(8) Å].[3] The mean deformation from 180° of the internal C≡C−C angle, 53.1°, is similar to those in $Pt(\eta^2-C_6H_8)(PPh_3)_2$[3] and in $Zr(\eta^5-C_5H_5)_2(\eta^2-C_6H_8)(PMe_3)$.[7]

Table 1. Selected Interatomic Distances (Å) and Angles (deg) in $Ni(\eta^2-C_6H_8)$(dcpe) (2)

Ni−P(1)	2.139(1)	Ni−P(2)	2.138(1)
Ni−C(1)	1.875(4)	Ni−C(2)	1.867(4)
P(1)−C(11)	1.860(4)	P(2)−C(21)	1.863(4)
P(1)−C(111)	1.856(4)	P(2)−C(211)	1.852(4)
P(1)−C(121)	1.854(4)	P(2)−C(221A)	1.865(7)
C(1)−C(2)	1.272(5)	P(2)−C(221B)	1.875(7)
C(1)−C(6)	1.504(6)	C(2)−C(3)	1.481(6)
P(1)−Ni−P(2)	91.33(4)	C(1)−Ni−C(2)	39.7(2)
P(1)−Ni−C(1)	152.6(1)	P(2)−Ni−C(2)	155.6(1)
P(1)−Ni−C(2)	112.8(1)	P(2)−Ni−C(1)	116.1(1)
Ni−P(1)−C(11)	108.5(1)	Ni−P(2)−C(21)	106.9(1)
Ni−P(1)−C(111)	118.2(1)	Ni−P(2)−C(211)	120.1(1)
Ni−P(1)−C(121)	117.4(1)	Ni−P(2)−C(221A)	123.4(2)
		Ni−P(2)−C(221B)	112.0(2)
C(11)−P(1)−C(111)	103.4(2)	C(21)−P(2)−C(211)	100.9(2)
C(11)−P(1)−C(121)	103.8(2)	C(21)−P(2)−C(221A)	107.2(2)
		C(21)−P(2)−C(221B)	99.5(3)
C(111)−P(1)−C(121)	103.9(2)	C(211)−P(2)−C(221A)	95.7(2)
		C(211)−P(2)−C(221B)	114.2(3)
Ni−C(1)−C(2)	69.8(2)	Ni−C(2)−C(1)	70.5(2)
Ni−C(1)−C(6)	164.7(3)	Ni−C(2)−C(3)	161.1(3)
C(2)−C(1)−C(6)	125.5(4)	C(1)−C(2)−C(3)	128.4(4)

Table 2. Crystallographic Data for $Ni(\eta^2-C_6H_8)$(dcpe) (2)[a]

chem formula	$C_{32}H_{56}NiP_2$
fw	561.44
cryst system	monoclinic
space group	$P2_1/n$
a (Å)	10.006(1)
b (Å)	17.772(1)
c (Å)	17.721(1)
β (deg)	90.27(1)
V (Å^3)	3151.2(4)
Z	4
D_{calc} (g cm^{-3})	1.183
μ[Cu Kα] (cm^{-1})	19.9
T (°C)	20(1)
cryst dimens (mm)	0.34 × 0.14 × 0.17
X radiation	Cu Kα
λ (Å)	1.5418
data range, deg in 2θ	4−128
no. unique data	5241
no. data refined	3932 [$I > 3\sigma(I)$]
no. variables	308
no. restraints	42
R	0.048
R_w	0.056
GOF	1.70
F(000)	1224

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum(wF_o)^2\}^{1/2}$; GOF = $\{\sum w(|F_o| - |F_c|)^2/(\text{no. ref} - \text{no. var})\}^{1/2}$.

Reactions of the Cyclohexyne Nickel Complexes. In general, the products of reaction of complex **2** (Scheme 2) are more stable and retain the C_6H_8

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(31) Bennett, M. A.; Warnock, G. F. Unpublished work, cited in Bennett, M. A.; Schwemlein, H. P. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1296.

(32) Lu, Z.; Abboud, K. A.; Jones, W. M. *Organometallics* **1993**, *12*, 1471.

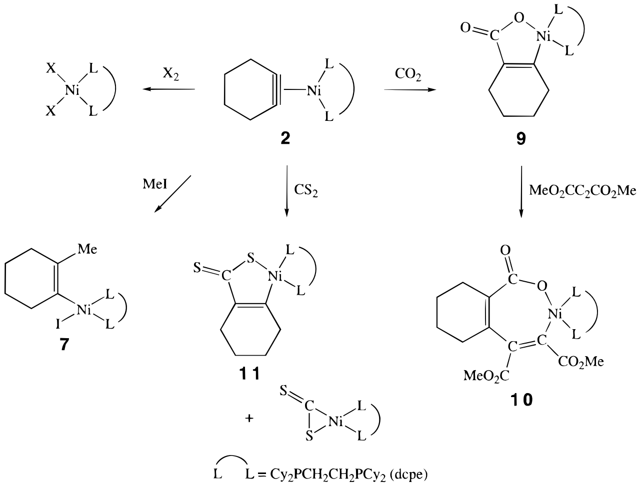
(33) Ittel, S. D.; Ibers, J. A. *Adv. Organomet. Chem.* **1976**, *14*, 33.

(34) Pörschke, K. R.; Tsay, Y.-H.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 323.

(35) Rosenthal, U.; Schulz, W.; Görls, H. *Z. Anorg. Allgem. Chem.* **1987**, *550*, 169.

(36) Rosenthal, U.; Oehme, G.; Görls, H.; Burlakov, V. V.; Polyakov, A. V.; Yanovskii, A. I.; Struchkov, Yu. T. *J. Organomet. Chem.* **1990**, *389*, 251.

Scheme 2. Oxidative Addition and Insertion Reactions of Ni(η^2-C_6H_8)(dcpe) (2)



fragment more readily than those of complexes **1** and **3**, containing monodentate tertiary phosphines.

Complex **2** reacted immediately with an equimolar amount of methyl iodide to give the (2-methylcyclohexenyl)iodonickel(II) complex NiI(2-MeC_6H_8)(dcpe) (**7**), which was isolated as an orange, air-stable powder in 64% yield. A small amount of NiI_2(dcpe) was also formed, as shown by the presence of a singlet at δ 95.2 in the $^{31}P\{^1H\}$ NMR spectrum. Compound **6** is easily soluble in benzene and THF, but is unstable in chlorinated solvents, even in an inert atmosphere. The structure follows from the NMR data: the $^{31}P\{^1H\}$ NMR spectrum shows an AB quartet (δ 57.7, 60.4; $^2J_{PP} = 9$ Hz), and the ^1H NMR spectrum shows a singlet at δ 2.4, due to the methyl group, in addition to broad, overlapping multiplets in the region δ 1.0−3.0 due to the methylene protons of the 2-methylcyclohexenyl and dcpe ligands.

Complex **3** reacted with methyl iodide to give an oil whose ^1H NMR spectrum showed a singlet at δ 2.4, suggestive of the presence of the 2-methylcyclohexenyl complex NiI(2-MeC_6H_8)$(PEt_3)_2$ (**8**). The $^{31}P\{^1H\}$ NMR spectrum, however, showed three singlets at δ 9.4, 10.8, and 12.4 in a ratio of about 1:10:6. The first and last are probably due to $NiI_2(PEt_3)_2$ and *trans*-NiI(Me)-$(PEt_3)_2$, respectively, as shown by comparison with authentic samples. Attempts to obtain a pure sample of **8** by fractional crystallization at low temperatures were unsuccessful. The reactions of **2** and **6** with methyl iodide are generally similar to those of Pt(η^2-C_6H_8)L_2 ($L_2 = 2PPh_3$, dppe), although there was no evidence for an intermediate product of oxidative addition to nickel corresponding to PtI(Me)(η^2-C_6H_8)$(PPh_3)_2$, which is the first detectable species formed from Pt(η^2-C_6H_8)$(PPh_3)_2$ and methyl iodide.[37]

Complex **2** reacted readily with bromine or iodine to form NiX_2(dcpe) (X = Br, I) and, presumably, the 1,2-dihalocyclohexene. In contrast to the behavior of Pt-(η^2-C_6H_8)L_2, there was no evidence for the expected intermediates NiX(2-XC_6H_8)(dcpe) [X = Br(**6**), I], probably because their Ni−C σ-bonds are rapidly cleaved by halogens.

Complex **2** reacted readily with CO_2 at room temperature and pressure to form the insertion product Ni{$C_6H_8C(O)O$}(dcpe) (**9**) in high yield as a yellow, air-stable solid; a similar product is formed from Ni(η^2-C_6H_4)(dcpe) and CO_2.[12] Compound **9** shows a parent ion peak in its EI mass spectrum, together with a fragment due to Ni(dcpe). The IR spectrum contains a strong ν(C=O) band at 1620 cm^{-1} due to the carboxylate group and a weak band at 1555 cm^{-1} due to ν(C=C). The ester carbon atom appears in the $^{13}C\{^1H\}$ NMR spectrum at δ 185.0, the carbon atom σ-bonded to nickel occurs as a ^{31}P-coupled doublet of doublets at δ 166.2, and a singlet at δ 128.6 can be assigned to the remaining vinyl carbon atom. The $^{31}P\{^1H\}$ NMR spectrum shows an AB quartet ($^2J_{PP}$ = 34 Hz) arising from *cis*-phosphorus atoms. A solution of complex **9** in benzene reacted with CO at room temperature and pressure and with 3-hexyne at 80 °C to give, respectively, $Ni(CO)_2$-(dcpe) and Ni(η^2-EtC_2Et)(dcpe); the fate of the organic fragment has not been investigated.

Dimethyl acetylenedicarboxylate inserted into the Ni−C σ-bond of **9** to give the seven-membered metallacycle Ni{$C(CO_2Me)$=$C(CO_2Me)C_6H_8C(O)O$}(dcpe) (**10**), which was isolated in 57% yield as an amber solid. It is air-stable in the solid state and stable in solution in the absence of air. The structural assignment rests on spectroscopic data. The $^{13}C\{^1H\}$ NMR spectrum shows three singlets at δ 173.6, 175.0, and 186.0 due to the carbonyl carbon atoms and a pair of doublets of doublets, arising from ^{31}P coupling, at δ 163.5 and 175.1, assignable to the *C*(CO_2Me) groups. The olefinic carbon atoms of the cyclohexene ring appear as singlets at δ 133.5 and 135.8. The inequivalent methoxyl groups give rise to a pair of methyl singlets at δ 3.50 and 4.70 in the ^1H NMR spectrum and at δ 51.4 and 52.7 in the ^{13}C NMR spectrum. There is an AB quartet in the ^{31}P-$\{^1H\}$ NMR spectrum ($^2J_{PP}$ = 34 Hz) indicative of cis-inequivalent phosphorus atoms. Complex **10** was recovered unchanged after heating in the solid state for 4 h at 102 °C; there was no evidence for thermal elimination of CO_2. The compound did decompose in refluxing xylene to give a yellow solid, which was shown by ^{31}P NMR spectroscopy to contain $Ni(CO)_2$(dcpe) in addition to other unidentified products.

The sulfur analogue of **10**, Ni{$C_6H_8C(S)S$}(dcpe) (**11**), is probably formed by reaction of **2** with CS_2 in benzene at room temperature, but it could not be separated from by products, including Ni(η^2-CS_2)(dcpe). The IR spectrum of **11** shows several bands in the ν(C=S) region (1100−1200 cm^{-1}), and the $^{31}P\{^1H\}$ NMR spectrum shows an AB quartet ($^2J_{PP}$ = 21 Hz).

Although complexes **1** and **3** readily react with both CO_2 and CS_2, we were unable to isolate insertion products analogous to **9** and **11**. The main product from **1** and CO_2 showed a sharp singlet at δ 24.5, apparently due to $Ni(PPh_3)_3$. There was no evidence for the formation of oligomers of cyclohexyne[27,28] and, when the reaction was carried out in the presence of tetraphenylcyclopentadienone or 2,5-diphenyl-3,4-isobenzofuran, the appropriate Diels−Alder adducts of cyclohexyne[29] were not formed. Other reactions in which cyclohexyne was apparently displaced from the coordination sphere were those of **1** with CS_2, **1** and **2** with acetylenes, and **1**−**3** with ethylene to give, respectively, [Ni(η^2-CS_2)-$(PPh_3)]_n$, [Ni(η^2-RC_2R)L_2] (R = Et, CO_2Me; $L_2 = 2PPh_3$, dcpe), and [Ni(η^2-C_2H_4)L_2] ($L_2 = 2PPh_3$, $2PEt_3$, dcpe).

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[37] Appleton, T. G.; Bennett, M. A.; Singh, A.; Yoshida, T. *J. Organomet. Chem.* **1978**, *154*, 369.

In the first two cases, the nickel-containing products were identified by comparison of their $^{31}P\{^1H\}$ NMR spectra with those of the complexes resulting from the displacement of ethylene from $Ni(\eta^2\text{-}C_2H_4)L_2$ by the appropriate ligand; the fate of the C_6H_8 moiety has not been determined.

Discussion

Cyclohexyne nickel(0) complexes $Ni(\eta^2\text{-}C_6H_8)L_2$ **1**−**3** can be made similarly to their platinum(0) analogues, but the coordinated C_6H_8 fragment seems to be more readily lost. This behavior is in apparent contrast to the trend in stability of the η^2-ethylene complexes of the d^{10} metals: the equilibrium constants governing eq 2 increase in the order Ni > Pt > Pd.[17] Although **2**

$$M(PPh_3)_3 + C_2H_4 \rightleftharpoons M(\eta^2\text{-}C_2H_4)(PPh_3)_2 + PPh_3 \quad (2)$$

undergoes stoichiometric insertion with CO_2 and CS_2, other π-acceptors induce rapid displacement of C_6H_8 from **1**−**3**, although not as free cyclohexyne. The π-acceptors may undergo double insertion into the Ni−C_6H_8 bond to give unstable nickelacycles that rapidly eliminate the organic moiety, leaving NiL_2. This type of pathway has been established in the reactions of alkynes with η^2-benzyne and (2,3-η)-naphthalyne nickel(0) complexes, $Ni(\eta^2\text{-}C_6H_4)L_2$[11] and $Ni(\eta^2\text{-}C_{10}H_6)L_2$.[38]

Experimental Section

All reactions were performed under nitrogen or argon with the use of standard Schlenk techniques. NMR spectra were recorded on Jeol FX-200 (^{1}H, 200 MHz), Varian XL-200 (^{1}H, 200 HMz; ^{13}C, 50.3 MHz; ^{31}P, 80.98 MHz) and Jeol FX-60 (^{31}P, 24.21 MHz) spectrometers. The ^{1}H and ^{13}C NMR chemical shifts are reported as δ-values relative to Me_4Si; ^{31}P NMR chemical shifts are reported relative to external 85% H_3PO_4, values of high frequency being positive. Infrared spectra were measured as KBr disks or as neat oils on KBr plates in the range 4000−250 cm^{-1} on a Perkin-Elmer 683 instrument. Mass spectra (EI) were recorded at 70 eV on a VG Micromass 7070 spectrometer. Melting points were measured in sealed tubes under nitrogen and are uncorrected. Elemental analyses were performed in-house.

Starting Materials. The compounds 1,2-dibromocyclohexene,[27] PMe_3,[39] $Me_2PCH_2CH_2PMe_2$(dmpe),[40] $Et_2PCH_2CH_2PEt_2$(depe),[40] $Cy_2PCH_2CH_2PCy_2$(dcpe),[40] $Ni(COD)_2$,[41] and $Ni(C_2H_4)L_2$ (2L = $2PPh_3$,[42−44] $2PEt_3$,[42] $2PCy_3$,[45] and dcpe[10]) were prepared by the appropriate literature methods. All other compounds were obtained from commercial suppliers.

Preparations. $Ni(\eta^2\text{-}C_6H_8)(PPh_3)_2$ (1). A solution containing $Ni(C_2H_4)(PPh_3)_2$ (1.72 g, 2.82 mmol) and 1,2-dibromocyclohexene (2.15 g, 8.96 mmol) in THF (30 mL) was added to 1% sodium amalgam that had been freshly prepared from sodium (0.59 g) and mercury (58.5 g), and the mixture was stirred for 15 h. The resulting yellow-brown solution was separated from the excess amalgam by centrifugation and was evaporated to dryness *in vacuo* to give a brown oil. The yellow solid that formed upon addition of ether was isolated by filtration, washed with hexane (10 mL), and dried *in vacuo* to give **1** (1.06 g, 56%). ^{1}H NMR (CD_2Cl_2): δ 1.71, 2.65 (each br s, CH_2), 6.9−7.6 (m, C_6H_5). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 27.3, 27.5 (each s, CH_2), 128.8, 131.6, 134.1 (each s, CH), 132.5 (t, CHP, $^1J_{PC}$ = 10 Hz), 138.1 (five line m, C≡C, separation between outer lines = 65 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 43.1 (s). IR (KBr, cm^{-1}) 1735 [s, ν(C≡C)]. Anal. Calcd for $C_{42}H_{38}P_2Ni$: C, 76.0; H, 5.8; Ni, 8.9. Found: C, 76.5, 74.2; H, 6.0, 6.1; Ni, 8.5.

$Ni(\eta^2\text{-}C_6H_8)$(dcpe) (2). This was prepared similarly to **1** from $Ni(C_2H_4)$(dcpe) (4.86 g, 9.55 mmol), 1,2-dibromocyclohexene (5.04g, 20.8 mmol), and 1% sodium amalgam [from sodium (2.3 g) and mercury (228 g)] in THF (70 mL). The yellow oil that was obtained after centrifugation and removal of solvent crystallized upon addition of ether at −30 °C. Recrystallization from ether at −30 °C gave **2** (3.25 g, 61%) as a yellow, crystalline solid (mp 140−145 °C (dec). ^{1}H NMR (CD_2Cl_2): δ 1.4−2.7 (m, CH, CH_2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 22.8 (t, CH_2P, $^1J_{PC}$ = 40 Hz), 26.7, 28.1, 29.5 (each s, CH_2), 30.6 (t, CH_2, $^2J_{PC}$ = 16 Hz), 35.5 (t, CHP, $^1J_{PC}$ = 21 Hz), 139.7 (five-line m, C≡C, separation between outer lines = 97 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 79.1 (s). IR (KBr, cm^{-1}): 1710 [s, ν(C≡C)]. EI mass spectrum: *m/z* 560 (parent ion). Anal. Calcd for $C_{32}H_{56}P_2Ni$: C, 68.5; H, 10.1; P, 11.0. Found: C, 68.1; H, 10.5; P, 11.0.

$Ni(\eta^2\text{-}C_6H_8)(PEt_3)_2$ (3). This was made similarly to **1** from $Ni(C_2H_4)(PEt_3)_2$ (0.34 g, 1.04 mmol), 1.2-dibromocyclohexene (0.62 g, 2.60 mmol), and 1% sodium amalgam [Na (0.25 g), Hg (24.7 g)] in THF (20 mL). Complex **3** was obtained as a yellow oil (0.25 g, 64%) that could not be crystallized from pentane at −78 °C. ^{1}H NMR (C_6D_6): δ 1.0 (t, CH_3), 1.2−2.2 (m, CH_2). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 9.0 (s, CH_3), 20.7 (t, CH_2P, $^1J_{PC}$ = 23 Hz), 27.6, 28.5 (each m, CH_2), 139.7 (five-line m, C≡C, separation between outer lines = 72 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 30.4 (s). IR (neat oil, cm^{-1}): 1715 [s, ν(C≡C)].

Attempted Preparation of $Ni(\eta^2\text{-}C_6H_8)(PCy_3)_2$ (4). A solution of $Ni(C_2H_4)(PCy_3)_2$ (4.09 g, 6.35 mmol) and 1,2-dibromocyclohexene (3.01 g, 12.5 mmol) in THF (30 mL) was added to 1% sodium amalgam that had been freshly prepared from sodium (1.45 g) and mercury (144 g), and the mixture was stirred for 24 h. After removal of the excess amalgam by centrifugation, the yellow-brown solution was evaporated to dryness *in vacuo* to give a brown oil that solidified upon addition of ether. The main product **4** was identified on the basis of its spectroscopic properties. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 21.4−35.0 (m, CH_2, CH, CHP), 139.7 (five-line m, C≡C, separation between outer lines = 80 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 49.1 (s). IR (neat oil, cm^{-1}): 1720 [m, ν(C≡C)]. The $^{31}P\{^1H\}$ NMR spectrum also showed peaks at δ 9.0, 37.0, 45.0, and 49.0, the last being due to **4**. Comparison with authentic materials showed the first three of these to be due to unchanged Cy_3P, $Ni(C_2H_4)(PCy_3)_2$, and $Ni(PCy_3)_3$, respectively.

Attempted Preparation of $Ni(\eta^2\text{-}C_6H_8)L_2$ [L = PPh_3 (1), PEt_3 (2)] from $Ni(COD)_2$. A solution of $Ni(COD)_2$ (1.76 g, 6.41 mmol), triphenylphosphine (3.35 g, 12.8 mmol), and 1,2-dibromocyclohexene (6.30 g, 26.6 mmol) in THF (80 mL) was added to sodium amalgam that had been freshly prepared from sodium (2.3 g) and mercury (225 g), and the mixture was stirred for 16 h. Workup as described earlier gave a brown oil that turned into a yellow-brown, air-sensitive solid. Spectroscopic data showed this to be a mixture of **1** and $Ni(PPh_3)_3$: $^{31}P\{^1H\}$ NMR (C_6D_6): δ 43.1 (s) (**1**), 24.3 (s) [$Ni(PPh_3)_3$]. IR (KBr, cm^{-1}): 1735 [s, ν(C≡C)]. A similar reaction between $Ni(COD)_2$, PEt_3, 1,2-dibromocyclohexene, and 1% Na/Hg gave impure **2**. Attempts to make $Ni(\eta^2\text{-}C_6H_8)L_2$ (L_2 = $2PMe_3$, $2PCy_3$, dmpe, depe, dcpe, and dppe) by this method failed.

Reaction of 1 with Bidentate Phosphines. A solution containing **1** (*ca.* 100 mg) and dcpe (*ca.* 50 mg) in benzene-d_6

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(38) Bennett, M. A.; Hockless, D. C. R.; Wenger, E. *Organometallics* **1995**, *14*, 2091.

(39) Luetkens, M. L., Jr.; Sattelberger, A. P.; Murray, H. H.; Basil, J. D.; Fackler, J. P., Jr. *Inorg. Synth.* **1989**, *26*, 7.

(40) Burt, R. J.; Chatt, J.; Hussain, W.; Leigh, G. J. *J. Organomet. Chem.* **1979**, *182*, 203.

(41) Schunn, R. A. *Inorg. Synth.* **1972**, *13*, 124.

(42) (a) Wilke, G.; Herrmann, G. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 549. (b) Herrmann, G. Ph.D. Thesis, Technische Hochschule Aachen, 1963.

(43) Ashley-Green, J.; Green, M.; Stone, F. G. A. *J. Chem. Soc. A* **1969**, 3019.

(44) Choi, H.; Hershberger, J. W.; Pinhas, A. R.; Ho, D. M. *Organometallics* **1991**, *10*, 2930.

(45) Jolly, P. W.; Jonas, K. *Inorg. Synth.* **1974**, *15*, 29.

(0.5 mL) was set aside at room temperature for 12 h. The $^{31}P\{^1H\}$ NMR spectrum of the resulting solution showed peaks at δ_P 79.2 (s) and 43.5 (s) in *ca.* 1:1 ratio, assigned to **2** and Ni(dcpe)$_2$, respectively. A similar reaction between **1** and dppe gave a mixture of Ni(η^2-C_6H_8)(dppe) [$^{31}P\{^1H\}$ NMR δ_P 60.2 (s); IR (KBr, cm^{-1}) 1720 [ν(C≡C)] and Ni(dppe)$_2$ (δ_P 43.9).

Reaction of 2 with Methyl Iodide. Methyl iodide (0.1 mL, 1.60 mmol) was added to **2** (0.38 g, 0.68 mmol) in benzene (10 mL), and the mixture was stirred for 15 min. The orange solution was evaporated *in vacuo* until solid began to precipitate. Addition of pentane (10 mL) gave an orange solid, which was isolated by filtration. The yield of NiI(2-MeC_6H_8)(dcpe) (**7**) [mp 140−141 °C (dec)] was 0.30 g (64%). ^1H NMR (C_6D_6): δ 1.0−2.8 (m, CH$_2$, CHP), 2.4 (s, Me). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 57.7, 60.4 (AB q, J = 9 Hz). MS: m/z 607 [NiI(dcpe)]$^+$. Anal. Calcd for $C_{33}H_{59}IP_2Ni$: C, 56.4; H, 8.5; P, 8.7. Found: C, 57.2; H, 8.6; P, 7.8.

A similar reaction between **3** and methyl iodide gave a mixture of *trans*-NiI(2-MeC_6H_8)(PEt$_3$)$_2$ (**8**) [^1H NMR (C_6D_6) δ 2.4 (s, Me); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 10.8 (s)], *trans*-NiI(Me)(PEt$_3$)$_2$ [$^{31}P\{^1H\}$ NMR (C_6D_6) δ 12.4 (s)], and *trans*-NiI$_2$(PEt$_3$)$_2$ [$^{31}P\{^1H\}$ NMR (C_6D_6) δ 9.3 (s)].

Reaction of 2 with Bromine. A solution of **2** (*ca.* 50 mg) in C_6D_6 (0.5 mL) in an NMR tube was treated with bromine (*ca.* 20 μL), and the mixture was set aside for 30 min. The only product detectable by ^{31}P NMR spectroscopy was NiBr$_2$(dcpe) [δ_P (C_6D_6) 86.9 (s)].

Reaction of 2 with 1,2-Dibromocyclohexene. A solution containing **2** (1.00 g, 1.78 mmol) and 1,2-dibromocyclohexene (1.60 g, 4.17 mmol) in THF (30 mL) was stirred for 48 h at room temperature. Removal of solvent gave a brown oil that could not be crystallized from ether at −78 °C. The $^{31}P\{^1H\}$ NMR spectrum showed an AB quartet at δ 61.4, 64.9, with $^2J_{PP}$ = 11.4 Hz, tentatively assigned to NiBr(2-BrC_6H_8)(dcpe) (**6**). A small amount of NiBr$_2$(dcpe) [δ_P 87.7] was also present. The brown oil was added to 1% sodium amalgam that had been freshly prepared from sodium (0.5 g) and mercury (49.5 g), and the mixture was stirred for 16 h. The excess amalgam was removed by centrifugation, and the resulting brown solution was evaporated to dryness *in vacuo*. The oil was redissolved in ether (20 mL) and, upon being cooled to −30 °C, gave yellow crystals, which were isolated by filtration and dried *in vacuo*. They were identified as **2** by $^{31}P\{^1H\}$ NMR and IR spectroscopy; the $^{31}P\{^1H\}$ NMR spectrum also showed a singlet at δ 56.1 due to an unidentified species, which constituted *ca.* 10% of the product.

Reaction of 1 with CO$_2$. (i) Carbon dioxide was bubbled through a solution of **1** (0.29 g, 0.35 mmol) in THF (30 mL) for 4 h. The resulting orange-brown solution was evaporated *in vacuo* to give a brown oil whose $^{31}P\{^1H\}$ NMR spectrum in C_6D_6 showed only a singlet at δ 24.3 due to Ni(PPh$_3$)$_3$. A sample of the oil was chromatographed on neutral alumina (activity III) and eluted with THF/hexane (1:1). The first, pale yellow fraction was evaporated to dryness, and the residue was recrystallized from hot hexane to give triphenylphosphine (80 mg), identified by its $^{31}P\{^1H\}$ NMR and mass spectra. Further elution gave triphenylphosphine oxide, identified similarly. There was no evidence for oligomers of cyclohexyne.

(ii) Carbon dioxide was bubbled through a solution containing **1** (0.70 g, 1.05 mmol) and 2,5-diphenyl-3,4-isobenzofuran (DPIBF) (0.45 g, 1.67 mmol) in THF (20 mL) at room temperature. Workup as described earlier gave only unchanged DPIBF, Ph$_3$P, and Ph$_3$PO. A similar result was obtained by the use of tetraphenylcyclopentadienone in place of DPIBF.

Reaction of 2 with CO$_2$. Carbon dioxide was bubbled through a solution of **2** (0.96 g, 1.71 mmol) in benzene (30 mL) for 3 h. The resulting precipitate was isolated by filtration, washed with hexane (2 × 10 mL), and dried *in vacuo* to give $\overline{\mathrm{Ni\{C_6H_8C(O)O}}\mathrm{\}(dcpe)}$ (**9**) (0.83 g, 81%) as a pale yellow solid. [mp 140−142 °C (dec)]. $^{13}C\{^1H\}$ NMR (CD$_2$Cl$_2$): δ 23.0−26.0 (m, CH$_2$, CH$_2$P, CHP), 128.6 (s, *C*CNi), 166.2 (dd, $^2J_{PC} + {}^2J_{P'C}$ = 107 Hz, C*C*Ni), 185.0 (br s, CO$_2$). $^{31}P\{^1H\}$ NMR (CD$_2$Cl$_2$): δ 66.1, 74.1 (AB q, J = 22 Hz). IR (KBr, cm^{-1}): 1620 [s, ν(C=O)], 1555 [w, ν(C=C)]. MS: m/z 605 (M$^+$), 480 [Ni(dcpe)$^+$]. Anal. Calcd for $C_{33}H_{56}OP_2Ni$: C, 65.5; H, 9.3; P, 10.1. Found: C, 65.9; H, 9.5; P, 9.0.

Reaction of 3 with CO$_2$. The $^{31}P\{^1H\}$ NMR spectrum of a solution of **3** in THF that had been treated with CO$_2$ for 15 min showed a singlet at δ 17.0, which may be due to an insertion product. After 2 h, this had been replaced by peaks at δ 7 (br m) and 46.0 (s) due to Ni(η^2-CO$_2$)(PEt$_3$)$_2$[46] and Et$_3$PO,[47] respectively, and the IR spectrum showed a band at 1620 cm^{-1} due to the former.

Reaction of 1 with CS$_2$. A solution of **1** (*ca.* 50 mg) in C_6D_6 (0.5 mL) in an NMR tube was treated with CS$_2$ (50 μL). After 5 h, the solution was centrifuged to remove some solid. The $^{31}P\{^1H\}$ NMR spectrum showed a peak at δ 24.8 (s) assigned to [Ni(η^2-CS$_2$)(PPh$_3$)]$_n$ by comparison with the spectrum of an authentic sample.[48]

Reaction of 2 with CS$_2$. To a solution of **2** (0.15 g, 0.27 mmol) in benzene (10 mL) was added CS$_2$ (50 μL, 0.84 mmol), and the mixture was stirred at room temperature for 12 h. The brown solid that deposited was isolated by filtration, washed with hexane (10 mL), and dried *in vacuo*. The $^{31}P\{^1H\}$ NMR spectrum in C_6D_6 showed AB quartets at δ 71.4, 75.3 (J = 21 Hz) and at δ 58.8, 64.0 (J = 8 Hz), which are assigned tentatively to $\overline{\mathrm{Ni\{C_6H_8C(S)S}}\mathrm{\}(dcpe)}$ and Ni(η^2-CS$_2$)(dcpe); there were also some unidentified peaks.

Reactions of Cyclohexyne Nickel(0) Complexes with Alkenes and Alkynes. (i) A solution of **1** (0.26 g, 0.38 mmol) in THF (20 mL) was treated with dimethyl acetylenedicarboxylate (71 μL, 0.58 mmol), and the mixture was stirred for 5 h. Removal of solvent *in vacuo* gave a brown oil, which was identified as Ni(MeO$_2$CC$_2$CO$_2$Me)(PPh$_3$)$_2$ by comparison with an authentic sample[49] [$^{31}P\{^1H\}$ NMR (C_6D_6) δ 38.8 (s)]. The complex Ni(MeO$_2$CC$_2$CO$_2$Me)(dcpe) [$^{31}P\{^1H\}$ NMR (C_6D_6) δ 74.8 (s)] was formed similarly from **2** and dimethyl acetylenedicarboxylate.

(ii) A solution of **1** (0.08 g, 0.12 mmol) in C_6D_6 (0.5 mL) was treated with 3-hexyne (15 μL, 0.13 mmol) and heated for 4 h at 70 °C. The $^{31}P\{^1H\}$ NMR spectrum showed a singlet at δ 39.9 assigned to Ni(EtC$_2$Et)(PPh$_3$)$_2$ by comparison with the spectrum of an authentic sample.[49] The complex Ni(EtC$_2$Et)(dcpe) [$^{31}P\{^1H\}$ NMR (C_6D_6) δ 69.7 (s)] was formed similarly from **2** and 3-hexyne at 70 °C.

(iii) A stream of ethylene was passed through a solution of **1** (0.25 g, 0.38 mmol) in THF (20 mL) for 12 h, giving a yellow solution. The yellow solid that remained after the solvent had been removed *in vacuo* was identified as Ni(C_2H_4)(PPh$_3$)$_2$ [$^{31}P\{^1H\}$ NMR (C_6D_6) δ 33.6]. A small amount of Ni(PPh$_3$)$_3$ [δ_P 24.2 (s)] was also present.

(iv) A solution of **2** (0.47 g, 0.83 mmol) in benzene (15 mL) was saturated with ethylene and left under an ethylene atmosphere at 80 °C for 72 h. The resulting yellow solution was evaporated to dryness *in vacuo* to leave a yellow solid, which was identified as Ni(C_2H_4)(dcpe) [$^{31}P\{^1H\}$ NMR (C_6D_6) δ 62.7 (s)].

Reaction of 9 with Dimethyl Acetylenedicarboxylate. A solution of **9** (0.44 g, 0.73 mmol) in THF (25 mL) was treated with dimethyl acetylenedicarboxylate (0.20 mL, 1.63 mmol), and the mixture was stirred for 4 h. The resulting amber precipitate was isolated by filtration and washed twice with

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[46] Aresta, M.; Nobile, C. F. *J. Chem. Soc., Dalton Trans.* **1977**, 708.

[47] Hays, H. R.; Peterson, D. J. in *Organic Phosphorus Compounds*; Kosolapoff, G., Maier, L., Eds.; Wiley: New York, 1972; Vol. 3, p 430.

[48] Uhlig, E.; Poppitz, W. *Z. Chem.* **1979**, *19*, 191.

[49] Rosenthal, U.; Oehme, G.; Burlakov, V. V.; Petrovskii, P. V.; Shur, V. B.; Vol'pin, M. E. *J. Organomet. Chem.* **1990**, *391*, 119.

hexane (10 mL) to give $\overline{\text{Ni}\{\text{C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})\{\text{C}_6\text{H}_8\text{C}(\text{O})\text{O}}\}$(dcpe) (**10**) (0.31 g, 57%) [mp 148−150 °C (dec)]. ^{1}H NMR (CD_2Cl_2): δ 1.2−2.6 (m, CH_2, CH_2P, CHP), 3.5(s, OMe), 3.7(s, OMe). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 23.0−37.0 (m, CH_2, CH_2P, CHP), 51.3, 51.4 (each s, OMe), 133.5, 135.6 (each s, C=C), 163.6 (dd, $^3J_{PC} + {}^3J_{P'C} = 12$ Hz, *C*CNi), 171.5 (dd, $^2J_{PC} + {}^2J_{P'C} = 106$ Hz, C*C*Ni), 173.6, 175.0 (each s, CO_2Me), 186.0 (s, CO_2). ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 65.5, 68.4 (AB q, $J = 35$ Hz). IR (KBr, cm^{-1}): 1710 (s), 1695 (s), 1640 (s) [ν(C=O)], 1555 (w) [ν(C=C)]. MS: m/z 702 $[\text{M} - \text{CO}_2]^+$. Anal. Calcd for $C_{39}H_{62}O_6P_2Ni$: C, 62.6: H, 8.3; P, 8.3. Found: C, 62.6; H, 8.4; P, 7.8.

Crystallography. A cross section cut from a yellow needle of Ni(η^2-C_6H_8)(dcpe) (**2**) was mounted on a Philips PW1100/20 diffractometer that was equipped with a graphite monochromator and used Cu Kα radiation. Lattice parameters were determined by least-squares analysis of the 2θ angles of 25 reflections $66 < 2\theta < 76°$ [λ(Cu Kα) = 1.5418 Å]. Crystallographic data are given in Table 2. Intensity data for reflections h, k, $\pm l$ with $3 < 2\theta < 128°$ ($0 \le h \le 11$, $0 \le k \le 20$, $-20 \le l \le 20$) were collected using θ−2θ scans of width $(1.0 + 0.142 \tan\theta)°$ in θ at a rate of 3° min^{-1} in θ, with background counts of 5 s on each side of every scan. Three check reflections measured every 90 min showed a 9% decrease in intensity during data collection, and data were corrected accordingly.[50] Data were also corrected for absorption (transmission range 0.639−0.784).

The structure was solved by Patterson synthesis and ΔF synthesis (SHELXS-86).[51] Disorder was evident in cyclohexyl group C(221)−C(226) and in atoms C(4) and C(5) of the cyclohexyne group. Each of these atoms was considered to be disordered over two sites of occupancy of 0.5, and in subsequent least-squares refinement, Waser restraints[52] were imposed on bonds and angles involving them. Anisotropic and isotropic displacement factors were employed for full-occupancy and half-occupancy non-hydrogen atoms, respectively. Hydrogen atoms were placed at calculated positions [r(C−H) = 0.95 Å, tetrahedral at the carbon atoms] and were not refined. Refinement was continued until all shift:error ratios were less than 0.04.

Least-squares refinement was performed by the use of full-matrix methods, the function $\sum w(|F_o| - |F_c|)^2$, where $w = [\sigma^2(F) + (0.0009)F^2]^{-1}$, being minimized. Maximum and minimum heights in a final difference map were 0.44 and −0.46 e Å^{-3}, respectively, the major features being in the vicinity of disordered C(4) and C(5). Data reduction and refinement computations were performed with XTAL3.0[53] ; atomic scattering factors for neutral atoms and real and imaginary dispersion terms were taken from ref 54 . Final parameters for the non-hydrogen atoms are given in Table 3.

Table 3. Atomic Coordinates and Equivalent Istropic Displacement Parameters[a] for the Non-Hydrogen Atoms in Ni(η^2-C_6H_8)(dcpe) (2)

	x/a	y/b	z/c	$U_{eq}{}^a/U$, Å^2
Ni	0.40408(6)	0.61136(3)	0.27862(3)	0.0477(2)[a]
P(1)	0.34903(10)	0.53969(5)	0.18662(5)	0.0513(3)[a]
P(2)	0.60997(9)	0.58151(5)	0.26694(5)	0.0526(3)[a]
C(1)	0.3640(4)	0.6789(2)	0.3566(2)	0.055(1)[a]
C(2)	0.2571(4)	0.6570(2)	0.3243(2)	0.058(1)[a]
C(3)	0.1173(4)	0.6776(3)	0.3421(3)	0.090(2)[a]
C(4A)[b]	0.1254(8)	0.7143(5)	0.4235(4)	0.077(2)
C(4B)[b]	0.1175(9)	0.7487(5)	0.3871(5)	0.098(3)
C(5A)[b]	0.2393(8)	0.7710(5)	0.4299(6)	0.079(3)
C(5B)[b]	0.2230(8)	0.7454(7)	0.4485(5)	0.100(4)
C(6)	0.3717(5)	0.7341(3)	0.4208(3)	0.085(2)[a]
C(11)	0.5039(4)	0.4993(2)	0.1454(2)	0.065(1)[a]
C(111)	0.2635(4)	0.5827(2)	0.1041(2)	0.055(1)[a]
C(112)	0.3334(5)	0.6547(2)	0.0791(2)	0.073(2)[a]
C(113)	0.2557(5)	0.6954(2)	0.0165(3)	0.081(2)[a]
C(114)	0.2301(5)	0.6438(3)	−0.0496(2)	0.089(2)[a]
C(115)	0.1600(5)	0.5730(3)	−0.0254(2)	0.085(2)[a]
C(116)	0.2386(5)	0.5313(2)	0.0360(2)	0.072(2)[a]
C(121)	0.2458(4)	0.4559(2)	0.2085(2)	0.058(1)[a]
C(122)	0.3087(5)	0.4131(2)	0.2744(2)	0.071(2)[a]
C(123)	0.2222(6)	0.3466(3)	0.3007(3)	0.086(2)[a]
C(124)	0.0818(6)	0.3716(3)	0.3183(3)	0.092(2)[a]
C(125)	0.0188(5)	0.4104(3)	0.2515(3)	0.084(2)[a]
C(126)	0.1020(4)	0.4778(2)	0.2267(2)	0.073(2)[a]
C(21)	0.6159(4)	0.4968(2)	0.2051(2)	0.065(1)[a]
C(211)	0.7065(4)	0.5481(2)	0.3499(2)	0.063(1)[a]
C(212)	0.6270(5)	0.4898(3)	0.3926(3)	0.087(2)[a]
C(213)	0.7048(6)	0.4586(3)	0.4607(3)	0.098(2)[a]
C(214)	0.7487(6)	0.5207(3)	0.5120(3)	0.098(2)[a]
C(215)	0.8263(6)	0.5792(3)	0.4701(3)	0.097(2)[a]
C(216)	0.7482(5)	0.6106(2)	0.4027(3)	0.075(2)[a]
C(221A)[b]	0.7405(7)	0.6480(3)	0.2325(4)	0.052(2)
C(221B)[b]	0.7024(7)	0.6498(4)	0.2057(4)	0.061(2)
C(222A)[b]	0.7066(8)	0.7279(4)	0.2542(5)	0.057(2)
C(222B)[b]	0.6798(8)	0.7301(4)	0.2287(5)	0.070(3)
C(223A)[b]	0.8091(9)	0.7842(4)	0.2254(4)	0.081(3)
C(223B)[b]	0.7476(8)	0.7862(4)	0.1763(5)	0.082(3)
C(224A)[b]	0.8439(10)	0.7727(5)	0.1413(5)	0.084(3)
C(224B)[b]	0.8965(9)	0.7707(5)	0.1710(6)	0.096(3)
C(225A)[b]	0.8773(9)	0.6927(5)	0.1227(5)	0.083(3)
C(225B)[b]	0.9206(10)	0.6915(5)	0.1480(6)	0.095(4)
C(226A)[b]	0.7662(8)	0.6406(4)	0.1477(4)	0.075(2)
C(226B)[b]	0.8512(7)	0.6338(4)	0.1989(5)	0.074(2)

[a] $U_{eq} = \frac{1}{3}\sum_i \sum_j U_{ij} a_i{}^* a_j{}^* \mathbf{a_i a_j}$. [b] Occupancy, 0.5.

Supporting Information Available: Lists of hydrogen atom parameters, atomic displacement parameters, all bond lengths and bond angles for non-hydrogen atoms, distances, angles, and torsion angles involving hydrogen atoms, and least-squares planes (23 pages). Ordering information is given on any current masthead page.

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(50) Churchill, M. R.; Kalra, K. L. *Inorg. Chem.* **1974**, *13*, 1427.

(51) Sheldrick, G. M. SHELXS-86. In *Crystallographic Computing 3*; Sheldrick, G. M., Krüger, C., Goddard, R., Eds; Oxford University Press: Oxford, England, 1985; pp. 175−189.

(52) (a) Waser, J. *Acta Crystallogr.* **1963**, *16*, 1091. (b) Olthof-Hazekamp, R. "CRYLSQ" in ref 53.

(53) Hall, S. R., Stewart, J. M., Eds. *XTAL3.0 Reference Manual*; Universities of Western Australia and Maryland, Lamb: Perth, 1990.

(54) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 99−101, 149−150 (Present distributor: Kluwer Academic Publishers, Dordrecht, The Netherlands).