# Ligand Displacement Reactions. Part V.[1] The Mechanisms of Displacement of Bidentate Olefins from Olefin(tetramethyl-1,4-benzoquinone)-nickel(0) Complexes by Trimethyl Phosphite

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Tributylphosphine reacts with the complexes olefin(tetramethyl-1,4-benzoquinone)nickel (olefin = cyclo-octatetraene or cyclo-octa-1,5-diene) to give bis(tributylphosphine)(tetramethyl-1,4-benzoquinone)nickel. With trimethyl phosphite the olefin complexes give tetrakis(trimethyl phosphite)nickel and, although intermediates cannot be detected, it is shown that displacement of the olefin precedes that of the quinone. The rate laws found for the reactions of trimethyl phosphite (P) with various olefin complexes (C) are for cyclo-octa-1,5-diene, rate = $\{k_1[C][P] + k_2[C][P]^2\}/(1 + k_3[P])$; for cyclo-octatetraene and norborna-2,5-diene, rate = $k_1[C][P] + k_2[C][P]^2$; for *endo*-dicyclopentadiene rate = $k_1[C][P]$. The reactions of trimethyl phosphite with bis(tetramethyl-1,4-benzoquinone)nickel and of tributylphosphine with the cyclo-octa-1,5-diene complex have rate = $k_1[C][P]$. The results are accommodated by a mechanism which involves initial bimolecular reaction of (C) and (P) to form an intermediate (A) in which the olefin is monodentate. Intermediate (A) can undergo unimolecular reversion to (C) and (P), unimolecular loss of olefin, or bimolecular reaction with (P) with loss of olefin. Subsequent reactions with trimethyl phosphite are fast. Stationary state theory applied to [A] gives a rate equation of the same form as that found for reaction of the cyclo-octa-1,5-diene complex with trimethyl phosphite. The rate laws for the other complexes are limiting forms of this equation. Primary rate constants are derived and the rate of initial reaction of (P) with (C) is shown to depend on olefin in the order: (tetramethyl-1,4-benzoquinone) $\ll$ cyclo-octa-1,5-diene < *endo*-dicyclopentadiene < norborna-2,5-diene and cyclo-octatetraene.

EARLIER papers of this series[1] describe the kinetics of displacement of arenes and cycloheptatriene from their metal(0) complexes by monodentate phosphorus bases. Although these $\pi$-donor ligands are usually regarded as polydentate, the donor sites are very strongly interdependent because of electron delocalisation and because of the rigidity of the essentially planar structures of the donor region. We now describe a study of the displacement of several common bidentate olefins and we show that the greater independence of the donor sites in such molecules can complicate the kinetics considerably, and that this can provide detailed information about the mechanism of the reaction.

## EXPERIMENTAL

Manipulations were made under dry nitrogen in a dry-bag or by use of Schlenk tube techniques. Solvents were dried, deoxygenated with a stream of nitrogen, and distilled through a Vigreux column. Reagent grade dienes were treated similarly except for *endo*-dicyclopentadiene which was purified by conversion into cyclopentadiene; this was allowed to dimerise in the dark during 1 month. Cyclo-octatetraene (Fluka Ltd.) was stored at −10°, and filtered and deoxygenated immediately before use. Tetramethyl-1,4-benzoquinone was obtained as yellow needles, m.p. 110—111°, from 1,2,4,5-tetramethylbenzene.[2] Trimethyl phosphite, tributyl phosphite, and tributylphosphine were fractionally distilled and stored under nitrogen. M.p.s were determined on a Kofler hot stage apparatus and i.r. spectra of complexes in Nujol mulls were obtained with a Perkin-Elmer 337 spectrophotometer.

The olefin complexes listed in Table 1 and bis(tetramethyl-1,4-benzoquinone)nickel were prepared by the methods of Schrauzer *et al.*[3]

*Characterisation of Reactions and Products.*—A Perkin-Elmer R10 spectrometer was used to obtain 60 MHz $^1$H n.m.r. spectra at 33·5°. I.r. spectra of solutions contained in 0·1-mm sodium chloride cells were determined with a Perkin-Elmer 237 spectrometer. A Unicam SP 800 spectrometer with a thermostatted cell block was used to obtain u.v. spectra of samples in Teflon-stoppered 1-cm silica cells.

*Reaction of Tributylphosphine with Cyclo-octa-*1,5-*diene-(tetramethyl-*1,4-*benzoquinone)nickel.*—In hydrocarbon solvents this reaction appeared to be represented by equation (1). The evidence is as follows.

$$[\mathrm{Ni(C_8H_{12})(C_{10}H_{12}O_2)}] + 2\mathrm{Bu_3P} \longrightarrow [\mathrm{Ni(Bu_3P)_2(C_{10}H_{12}O_2)}] + \mathrm{C_8H_{12}} \quad (1)$$

I.r. spectra (1500—1650 cm$^{-1}$) of a mixture of the cyclo-octa-1,5-diene complex (0·02M) and tributylphosphine (0·3M) in benzene recorded at 10—20 min intervals had an isosbestic point at 1548 cm$^{-1}$, and as the reaction progressed, ν(CO) for the complex at 1553 cm$^{-1}$ disappeared as a peak at 1540 cm$^{-1}$ [assigned to ν(CO) in the product] appeared. No peak at 1630 cm$^{-1}$ due to free tetramethyl-1,4-benzoquinone was detected. The reaction appeared to be complete after *ca.* 3 h and no further change in the spectrum occurred during a further 48 h.

Although the product could be isolated from the cyclo-octa-1,5-diene complex, we obtained a more satisfactory sample from a more labile complex. Cyclo-octatetraene-(tetramethyl-1,4-benzoquinone)nickel (1·1 g) and tributylphosphine (2·1 g) were allowed to react for 8 h at 30—40° in hexane (40 ml) with rigorous exclusion of air. The red solution obtained was filtered and evaporated and the residue was recrystallised from hexane. A red, very air-sensitive solid was obtained which gave nickel and phosphorus analyses corresponding well with the formula $[\mathrm{Ni(Bu_3P)_2(C_{10}H_{12}O_2)}]$ and which had ν(CO) 1540 cm$^{-1}$ (Table 1). (This complex has been briefly mentioned by Schrauzer.[4])

In the $^1$H n.m.r. spectra of a mixture of the cyclo-octa-1,5-diene complex (0·01M) and tributylphosphine (0·2M) in deuteriobenzene, the intensity of the resonance from the olefinic protons of the free diene (τ 4·4) increased in-

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[1] Part IV, A. Pidcock, J. D. Smith, and B. W. Taylor, *Inorg. Chem.*, 1970, **9**, 638.

[2] L. I. Smith, *Org. Synth*, 1943, Coll. Vol. 2, 254.

[3] G. N. Schrauzer and H. Thyret, *Z. Naturforsch.*, 1961, **16b**, 254; 1962, **17b**, 73.

[4] G. N. Schrauzer, *Adv. Organometalic Chem.*, 1964, **2**, 1.

tensity as the reaction progressed and other changes in the spectra were consistent with the production of the bis(phosphine)quinone complex (Table 1).

At the much lower concentration of complex (1—2 × $10^{-4}$M) necessary for spectrophotometry in the 280—450 nm region, the reaction (in heptane) appeared to have two stages. Initially an isosbestic point was present at 380 nm and a peak appeared which had a maximum intensity at 386 nm which was similar to that observed for the bis(phosphine)quinone complex (388 nm). The half-life of this stage, *ca.* 10—120 min, was dependent on the concentration of phosphine (2·1 × $10^{-2}$—3·7 × $10^{-1}$M). After *ca.* 30 min, the absorbance at all wavelengths started to decrease and it was found that the rate of this process was not reproducible and there was no clear dependence of the rate on the concentration of phosphine. It is probable that the second stage represents oxidation of the very air-sensitive bis(phosphine)quinone complex.

TABLE 1

Nickel complexes

| Complex | M.p.[a] Found | M.p.[a] Lit.[a] | $\nu$(CO)[b] $cm^{-1}$ | Found (%) C | Found (%) H | Calc. (%) C | Calc. (%) H |
|---|---|---|---|---|---|---|---|
| Cyclo-octa-1,5-diene(tetramethyl-1,4-benzoquinone)nickel[c] | 201° (decomp.) | 205° | 1550 | 64·9 | 7·3 | 65·3 | 7·3 |
| *endo*-Dicyclopentadiene(tetramethyl-1,4-benzoquinone)nickel | 135 (decomp.) | 137 | 1549 | 67·7 | 6·9 | 67·7 | 6·8 |
| Norborna-2,5-diene(tetramethyl-1,4-benzoquinone)nickel | 126 (decomp.) | 130 | 1442 | 64·6 | 6·6 | 64·8 | 6·4 |
| Cyclo-octatetraene(tetramethyl-1,4-benzoquinone)nickel | 162 (decomp.) | 165 | 1557 | 66·4 | 6·3 | 66·1 | 6·2 |
| Bis(tetramethyl-1,4-benzoquinone)nickel | 201 (decomp.) | 205 | 1580 | 62·4 | 6·4 | 62·0 | 6·3 |
| Bis(tributylphosphine)(tetramethyl-1,4-benzoquinone)nickel[d] | 76—80 | | 1540 | 60·0 | 9·1 | 65·0 | 10·4 |
| Tetrakis(trimethyl phosphite)nickel[e] | 70 | | | 25·0 | 7·2 | 26·0 | 6·5 |
| *cis*-Dichlorobis(tributylphosphine)nickel | 47—48 | | | | | | |

[a] In air. See ref. 3 for lit. m.p.s. [b] In Nujol. [c] $M^+$ 330, $M(^{58}Ni)$(Calc.) 330. [d] Found: Ni, 9·0; P. 9·83%. Calc: Ni, 9·1; P, 9·87%. Compounds of this type are difficult to analyse for C and H. The $^1$H n.m.r. spectrum gives the ratio of intensities of resonances from quinone methyl groups: resonances from tributylphosphine to be 4·8 (calc. 4·5). The quinone methyl groups give a doublet which is expected if $^2J$(PNiP′) is small. [e] $M^+$ 556, $M(^{58}Ni)$(Calc.) 556.

The u.v. spectra of mixtures of the cyclo-octa-1,5-diene complex (1—1·5 × $10^{-4}$M) and tributylphosphine (1—10 × $10^{-2}$M) in 1,2-dichloroethane had isosbestic points at 397 nm and the spectrum of the product, which was obtained after *ca.* 30 min, was identical with that of [$NiCl_2(Bu_3P)_2$]. Although linear plots of log ($D_t - D_\infty$) *vs* time were obtained, the rate constants were not reproducible and their dependence on the concentration of phosphine could not be determined. The reaction rates were greater than those in heptane. At a higher concentration of complex (2 × $10^{-2}$M) i.r. spectra (1500—1650 $cm^{-1}$) showed that even after 6 h the starting material was still present and that the quinone was probably mainly in the form of the bis(phosphine)-nickel complex (intense peak at 1540 $cm^{-1}$) with only a small peak at 1630 $cm^{-1}$ due to free quinone. After a further 48 h, the intensity of the peak due to free quinone had increased and that of the peak due to phosphine complex had decreased, but even after 200 h, reaction mixtures on a preparative scale had a band at 1540 $cm^{-1}$. From one such reaction we isolated crude [$NiCl_2(Bu_3P)_2$] (61%).

Since the rate of decomposition of the olefin complex in 1,2-dichloroethane was slow, the dependence of the reaction course on the initial concentration of complex suggested that phosphine-containing intermediates were reacting with an impurity in the solvent. Addition of small amounts of impurities identified by g.l.c. (ethanol and carbon tetrachloride) to reaction mixtures in benzene failed to produce substantial conversion into [$NiCl_2(Bu_3P)_2$]. The kinetics of the reactions at low complex concentrations were not reproducible and this system was not studied further.

*Reactions with Trimethyl Phosphite.*—The reactions of the olefin complexes and of bis(tetramethyl-1,4-benzoquinone)-nickel with trimethyl phosphite in hydrocarbon solvents gave tetrakis(trimethyl phosphite)nickel, free quinone, and free olefin. The tetrakis(phosphite) complex was isolated in poor yields from both cyclo-octa-1,5-diene(tetramethyl-1,4-benzoquinone)nickel and the bis(quinone)nickel complex after reaction with trimethyl phosphite in benzene. After evaporation of the solvent, the quinone was sublimed off at 40—50° at 0·01 mmHg, and the residue was recrystallised from methanol–water. Although the analytical data (Table 1) are not good, the $^1$H n.m.r. spectra of these samples were identical with that of a sample made by the method of Vinal and Reynolds[5] which had m.p. 70° (decomp.) (206—220° under nitrogen) [Found: C, 26·3; H, 6·5%; $M^+$ 555. Calc. for $C_{12}H_{36}NiO_{12}P_4$: C, 26·0; H, 6·5%; $M(^{57}Ni)$, 555].

In the $^1$H n.m.r. spectra of the cyclo-octa-1,5-diene complex (0·12M) and trimethyl phosphite (0·6M) in benzene the intensity of the resonances from the complexed quinone ($\tau$ 8·0$_5$), olefin ($\tau$ 6·5, $CH_2$ region only), and trimethylphosphite (d, $J$ 10 Hz, $\tau$ 6·7) decreased in intensity as resonances due to free quinone ($\tau$ 8·3), free olefin ($\tau$ 1·8), and [Ni{$(MeO)_3P$}$_4$] (complex pattern at $\tau$ 6·6—6·8) appeared. No other products or intermediates could be detected. I.r. spectra of reaction mixtures showed the formation of free quinone (band at 1630 $cm^{-1}$) and disappearance of complexed quinone (1553 $cm^{-1}$). The absence of appreciable concentrations of intermediates or of other products was also shown by the u.v. spectra (250—450 nm) of reaction mixtures. Isosbestic points were observed for the reactions in heptane, and for the reactions in toluene, where absorption by solvent obscures the isosbestic point, graphs of $D_t^{\lambda}$ *vs.* $D_t^{\lambda'}$ were linear to within experimental error. For the reaction of the cyclo-octa-1,5-diene complex, the isosbestic point at 274 nm was within 1 nm of that calculated from the spectra of the starting complex and the free quinone; [Ni{$(MeO)_3P$}$_4$] has negligible absorption in this region.

*Determination of Rates.*—Reaction mixtures were prepared for rate measurements by methods described previously.[6] For the reactions with trimethyl phosphite,

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[5] R. S. Vinal and S. T. Reynolds, *Inorg. Chem.*, 1964, **3**, 1062.

[6] A. Pidcock, J. D. Smith, and B. W. Taylor, *J. Chem. Soc.* (*A*), 1967, 872; A. Pidcock and B. W. Taylor, *ibid.*, p. 877.

optical densities at *ca.* 370 nm for the olefin complexes and 399 nm for the bis(quinone) complex were monitored with a Unicam SP 500 spectrophotometer fitted with a thermostatted cell block. Reactions with a half-life greater than *ca.* 1 min could be followed. Because it was necessary to determine the duration of the isosbestic point in the reaction of the cyclo-octa-1,5-diene complex with tributylphosphine, measurements were made with the SP 800 instrument as described before.

Initial concentrations of complexes (1—2 × $10^{-4}$M) were chosen to give changes in optical densities from *ca.* 0·75 to 0·02.

Computer programmes supplied by the University of Sussex Computing Centre were used for least-squares analysis of the results.

## RESULTS

Measurements of rates were made under pseudo-first-order conditions. Optical densities measured during the reaction ($D_t$) and after 10 half-lives ($D_\infty$) were used to construct plots of log ($D_t - D_\infty$) *vs.* time. These were linear to beyond 80% reaction and were used to obtain the pseudo-first-order rate constants, $k_{obs}$ (Table 2), for the disappearance of the complex (C). These were reproducible to within 2%. Because the product of the reaction of tributylphosphine and the cyclo-octa-1,5-diene complex was not stable under the conditions used, $D_\infty$ could not be determined directly and Guggenheim's method [7] was used to obtain the values of $k_{obs}$ in Table 2. For this reaction and for the reactions of trimethyl phosphite with *endo*-dicyclopentadiene(tetramethyl-1,4-benzoquinone)nickel and bis(tetramethyl-1,4-benzoquinone)nickel, plots of $k_{obs}$ against the concentration of phosphorus base [P] were linear.

TABLE 2

Pseudo-first-order rate constants for the reactions of olefin-(tetramethyl-1,4-benzoquinone)nickel(0) complexes with base (P) [a]

| $10^3$[P]/M | Temp. | $10^4k_{obs}$/s$^{-1}$ | $10^3$[P]/M | Temp. | $10^4k_{obs}$/s$^{-1}$ |
|---|---|---|---|---|---|
| (A) Olefin = cycloocta-1,5-diene, (P) = Bu$_3$P, in heptane | | | | | |
| 21·0 | $29{\cdot}6_0$° | 9·21 | 123 | $29{\cdot}6_0$° | 34·5 |
| 37·0 | $29{\cdot}6_0$ | 12·4 | 273 | $29{\cdot}6_0$ | 88 |
| 82·0 | $29{\cdot}6_0$ | 27·2 | 368 | $29{\cdot}6_0$ | 124 |
| (B) Olefin = cycloocta-1,5-diene, (P) = (MeO)$_3$P, in heptane | | | | | |
| 4·6 | $29{\cdot}6_0$° | 1·82 | 69·8 | $29{\cdot}6_0$° | 103·4 |
| 6·7 | $29{\cdot}6_0$ | 3·01 | 4·7 | $49{\cdot}6_0$ | 7·5 |
| 9·2 | $29{\cdot}6_0$ | 4·75 | 5·5 | $49{\cdot}6_0$ | 9·0 |
| 9·3 | $29{\cdot}6_0$ | 4·74 | 7·8 | $49{\cdot}6_0$ | 13·1 |
| 11·5 | $29{\cdot}6_0$ | 6·50 | 9·4 | $49{\cdot}6_0$ | 17·7 |
| 14·0 | $29{\cdot}6_0$ | 9·00 | 11·7 | $49{\cdot}6_0$ | 22·8 |
| 23·0 | $29{\cdot}6_0$ | 19·0 | 15·7 | $49{\cdot}6_0$ | 31·8 |
| 27·9 | $29{\cdot}6_0$ | 26·1 | 18·1 | $49{\cdot}6_0$ | 40·6 |
| 34·4 | $29{\cdot}6_0$ | 34·6 | 27·2 | $49{\cdot}6_0$ | 65·8 |
| 45·0 | $29{\cdot}6_0$ | 51·8 | 30·3 | $49{\cdot}6_0$ | 75·3 |
| 46·5 | $29{\cdot}6_0$ | 55·9 | 45·3 | $49{\cdot}6_0$ | 133 |
| (C) Olefin = cyclo-octa-1,5-diene, (P) = (MeO)$_3$P, in toluene [b] | | | | | |
| 4·3 | $29{\cdot}6_0$° | 0·14 | 68·1 | $40{\cdot}0_5$° | 31·3 |
| 6·5 | $29{\cdot}6_0$ | 0·29 | 69·1 | $40{\cdot}0_5$ | 31·7 |
| 9·1 | $29{\cdot}6_0$ | 0·57 | 69·1 | $40{\cdot}0_5$ | 31·9 |
| 21·6 | $29{\cdot}6_0$ | 2·2 | 91·1 | $40{\cdot}0_5$ | 48·8 |
| 32·6 | $29{\cdot}6_0$ | 4·4 | 91·2 | $40{\cdot}0_5$ | 49·3 |
| 43·1 | $29{\cdot}6_0$ | 6·8 | $103{\cdot}_6$ | $40{\cdot}0_5$ | 58·8 |
| 60·2 | $29{\cdot}6_0$ | 11·8 | $103{\cdot}_6$ | $40{\cdot}0_5$ | 58·9 |
| 81·6 | $29{\cdot}6_0$ | 19·6 | 5·5 | $49{\cdot}6_0$ | 1·94 |
| 86·2 | $29{\cdot}6_0$ | 21·1 | 17·5 | $49{\cdot}6_0$ | 9·0 |
| 90·4 | $29{\cdot}6_0$ | 23·6 | 19·1 | $49{\cdot}6_0$ | 9·4 |
| $100{\cdot}_4$ | $29{\cdot}6_0$ | 28·2 | 21·9 | $49{\cdot}6_0$ | 11·7 |
| $120{\cdot}_5$ | $29{\cdot}6_0$ | 36·5 | 32·3 | $49{\cdot}6_0$ | 18·6 |
| 151 | $29{\cdot}6_0$ | 50·9 | 39·1 | 24·3 | |
| 163 | $29{\cdot}6_0$ | 56·7 | 43·8 | $49{\cdot}6_0$ | 28·9 |
| 181 | $29{\cdot}6_0$ | 68·5 | 47·7 | $49{\cdot}6_0$ | 31·3 |
| 6·42 | $40{\cdot}0_5$ | 0·90 | 48·4 | $49{\cdot}6_0$ | 32·0 |
| 9·11 | $40{\cdot}0_5$ | 1·60 | 50·5 | $49{\cdot}6_0$ | 34·4 |
| 13·7 | $40{\cdot}0_5$ | 2·80 | 56·1 | $49{\cdot}6_0$ | 39·2 |
| 18·2 | $40{\cdot}0_5$ | 4·1 | 58·7 | $49{\cdot}6_0$ | 43·9 |
| 34·1 | $40{\cdot}0_5$ | 10·7 | 64·5 | $49{\cdot}6_0$ | 47·6 |
| 34·5 | $40{\cdot}0_5$ | 10·5 | 67·3 | $49{\cdot}6_0$ | 52·3 |
| 42·8 | $40{\cdot}0_5$ | 14·0 | 84·1 | $49{\cdot}6_0$ | 68·7 |
| 45·6 | $40{\cdot}0_5$ | 16·1 | 87·5 | $49{\cdot}6_0$ | 74·5 |
| 45·6 | $40{\cdot}0_5$ | 16·4 | 87·5 | $49{\cdot}6_0$ | 75·0 |
| 51·8 | $40{\cdot}0_5$ | 19·2 | 97·0 | $49{\cdot}6_0$ | 84·1 |
| 64·2 | $40{\cdot}0_5$ | 27·6 | 101·0 | $49{\cdot}6_0$ | 90·0 |
| (D) Olefin = cyclo-octa-1,5-diene, (P) = (BuO)$_3$P, in heptane | | | | | |
| 4·0 | $29{\cdot}6_0$° | 1·6 | 29·9 | $29{\cdot}6_0$° | 18·9 |
| 6·6 | $29{\cdot}6_0$ | 2·7 | 33·4 | $29{\cdot}6_0$ | 21·6 |
| 12·0 | $29{\cdot}6_0$ | 5·6 | 50·1 | $29{\cdot}6_0$ | 37·6 |
| 19·9 | $29{\cdot}6_0$ | 11·2 | 66·8 | $29{\cdot}6_0$ | 5·22 |
| 25·0 | $29{\cdot}6_0$ | 14·7 | $100{\cdot}_1$ | $29{\cdot}6_0$ | 96·7 |
| (E) Olefin = *endo*-dicyclopentadiene, (P) = (MeO)$_3$P, in toluene | | | | | |
| 6·6 | $29{\cdot}6_0$° | 12·8 | 6·8 | $40{\cdot}0_5$° | 33·3 |
| 6·6 | $29{\cdot}6_0$ | 13·3 | 9·1 | $40{\cdot}0_5$ | 42·2 |
| 8·1 | $29{\cdot}6_0$ | 18·2 | 12·1 | $40{\cdot}0_5$ | 57·2 |
| 9·9 | $29{\cdot}6_0$ | $23{\cdot}6_0$ | 14·3 | $40{\cdot}0_5$ | 66·9 |
| 16·5 | $29{\cdot}6_0$ | 38·2 | 18·2 | $40{\cdot}0_5$ | 85·6 |
| 32·9 | $29{\cdot}6_0$ | 74·0 | 5·6 | 49·6 | 47·0 |
| 40·7 | $29{\cdot}6_0$ | 99·3 | 8·4 | $49{\cdot}6_0$ | 74·0 |
| 49·5 | $29{\cdot}6_0$ | 117 | 11·2 | $49{\cdot}6_0$ | 95·0 |
| 3·7 | $40{\cdot}0_5$ | 16·1 | 16·8 | $49{\cdot}6_0$ | 14·3 |
| 6·4 | $40{\cdot}0_5$ | 28·5 | | | |
| (F) Olefin = norborna-2,5-diene, (P) = (MeO)$_3$P, in toluene | | | | | |
| 3·6 | $29{\cdot}6_0$° | 17·0 | 9·0 | $29{\cdot}6_0$° | 46·0 |
| 3·6 | $29{\cdot}6_0$ | 17·2 | 10·0 | $29{\cdot}6_0$ | 55·0 |
| 4·2 | $29{\cdot}6_0$ | 19·4 | 12·5 | $29{\cdot}6_0$ | 70·4 |
| 4·5 | $29{\cdot}6_0$ | 22·5 | 16·6 | $29{\cdot}6_0$ | 99·0 |
| 8·0 | $29{\cdot}6_0$ | 41·9 | 18·0 | $29{\cdot}6_0$ | 102 |
| 8·8 | $29{\cdot}6_0$ | 44·2 | 20·0 | $29{\cdot}6_0$ | 119 |
| (G) Olefin = cyclo-octatetraene, (P) = (MeO)$_3$P, in toluene | | | | | |
| 3·80 | $29{\cdot}6_0$° | 8·7 | 25·3 | $29{\cdot}6_0$ | 96·7 |
| 6·00 | $29{\cdot}6_0$ | 14·2 | 29·8 | $29{\cdot}6_0$ | 119 |
| 7·60 | $29{\cdot}6_0$ | 18·8 | 5·33 | $40{\cdot}1_0$ | 33·0 |
| 9·00 | $29{\cdot}6_0$ | 22·4 | 8·01 | $40{\cdot}1_0$ | 50·6 |
| 17·9 | $29{\cdot}6_0$ | 59·4 | 13·9 | $40{\cdot}1_0$ | 94·4 |
| 19·0 | $29{\cdot}6_0$ | 64·4 | 20·9 | $40{\cdot}1_0$ | 144 |
| (H) Olefin = tetramethyl-1,4-benzoquinone, (P) = (MeO)$_3$P, in toluene [c] | | | | | |
| 9·90 | $29{\cdot}6_0$° | 0·28 | 171 | $40{\cdot}0_5$° | 14·5 |
| 33·0 | $29{\cdot}6_0$ | 0·97 | 238 | $40{\cdot}0_5$ | 18·9 |
| 75·0 | $29{\cdot}6_0$ | 2·33 | 342 | $40{\cdot}0_5$ | 28·6 |
| 150 | $29{\cdot}6_0$ | 4·84 | 456 | $40{\cdot}0_5$ | 38·3 |
| 299 | $29{\cdot}6_0$ | 9·40 | 9·50 | $49{\cdot}7_0$ | 1·71 |
| 299 | $29{\cdot}6_0$ | 9·41 | 19·1 | $49{\cdot}7_0$ | 3·60 |
| 597 | $29{\cdot}6_0$ | 18·5 | 48·0 | $49{\cdot}7_0$ | 9·00 |
| 896 | $29{\cdot}6_0$ | 28·2 | 88·0 | $49{\cdot}7_0$ | 16·6 |
| 18·0 | $40{\cdot}0_5$ | 1·40 | 95·0 | $49{\cdot}7_0$ | 18·1 |
| 46·0 | $40{\cdot}0_5$ | 3·70 | 176 | $49{\cdot}7_0$ | 34·6 |
| 68·0 | $40{\cdot}0_5$ | 6·10 | 238 | $49{\cdot}7_0$ | 43·3 |
| 91·0 | $40{\cdot}0_5$ | 7·60 | 477 | $49{\cdot}7_0$ | 87·1 |

[a] Initial concentration of complexes *ca.* 1—2 × $10^{-4}$M. Experiments at $29{\cdot}9_0$° with [(MeO)$_3$P] = 5·59 × $10^{-4}$M in presence of: (a) cyclo-octa-1,5-diene (2·1 × $10^{-3}$M), $k_{obs}$ = (11·80 ± 0·04) × $10^{-4}$ s$^{-1}$; (b) tetramethyl-1,4-benzoquinone (2·1 × $10^{-3}$M), $k_{obs}$ = (12·02 ± 0·05) × $10^{-4}$ s; and (c) reaction with no additives, $k_{obs}$ = (11·91 ± 0·04) × $10^{-4}$ s$^{-1}$. Errors quoted are standard deviations for the first-order rate plot; the rate constants are identical to within the probable experimental error. [c] Reaction of bis(tetramethyl-1,4-benzoquinone)nickel.

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[7] A. A. Frost and R. G. Pearson, 'Kinetics and Mechanism,' 2nd. edn., Wiley, New York, 1961, ch. 3.

Least-squares analysis was used to fit the data to the equation $k_{obs} = k_0 + k_1[P]$, and since values of $k_0$ were always within two standard deviations of zero, the rate equation for these reactions over the concentration ranges of (P) studied is equation (2) (See Table 3).

$$\text{Rate} = k_1\,[C][P] \qquad (2)$$

(P) = $Bu_3P$, (C) = cyclo-octa-1,5-diene complex
(P) = $(MeO)_3P$, (C) = bis(quinone) complex
(P) = $(MeO)_3P$, (C) = *endo*-dicyclopentadiene complex

An example of this behaviour is given in Figure 1 where it is also shown that other reactions cannot be adequately represented by equation (2).

Linear plots of $k_{obs}/[P]$ *vs.* [P] were obtained for reactions of trimethyl phosphate with the (tetramethyl-1,4-benzoquinone)nickel complexes of norborna-2,5-diene and cyclo-octatetraene (Figure 2) and the results of least-squares fitting to the equation $k_{obs}/[P] = k_1 + k_2[P]$ are given in Table 3. The rate equation is therefore given by equation (3) for these reactions, but it is clear from

$$\text{Rate} = k_1[C][P] + k_2[C][P]^2 \qquad (3)$$

(P) = $(MeO)_3P$
(C) = norborna-2,5-diene and cyclo-octatetraene complex

Figure 2 that this does not adequately represent the data for the reaction of trimethyl phosphite with the cyclo-octa-1,5-diene complex. For this reaction it was found that one of the possible mechanisms (given in detail later) led to an equation of the form (4) and that the parameters

$$\text{Rate} = \{k_1[C][P] + k_2[C][P]^2\}/\{1 + k_3[P]\} \qquad (4)$$

(P) = $(MeO)_3P$ or $(BuO)_3P$
(C) = cyclo-octa-1,5-diene complex

$k_1$—$k_3$, determined by least-squares analysis, (Table 3) gave an accurate fit to the data (see Figure 1).

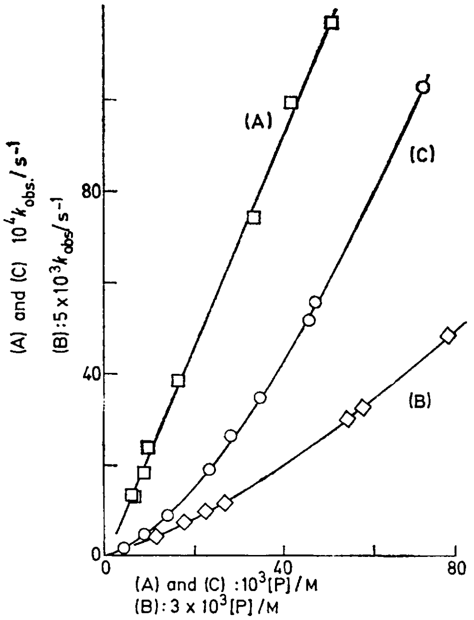


FIGURE 1 Dependence of $k_{obs}$ on [P] for the reaction of trimethyl phosphite at $29{\cdot}6_0$° with: (A) *endo*-dicyclopentadiene complex in toluene, (B) cyclo-octatetraene complex in toluene, and (C) cyclo-octa-1,5-diene complex in heptane (the curve drawn is derived from the parameters given in Table 3)

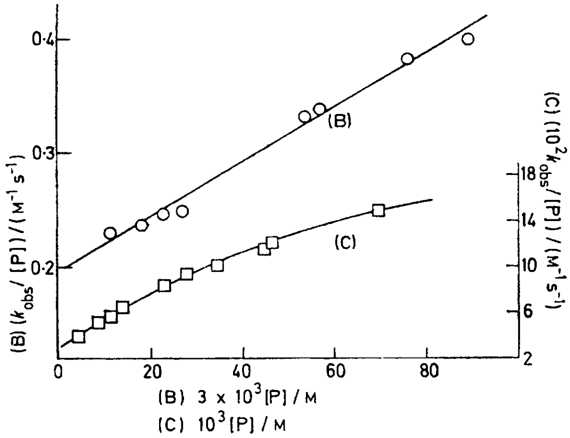


FIGURE 2 Dependence of $k_{obs}/[P]$ on [P] for the reactions of trimethyl phosphite at $29{\cdot}6_0$° with: (B) cyclo-octatetraene complex in toluene, and (C) cyclo-octa-1,5-diene complex in heptane

TABLE 3

Rate parameters defined by rate = $k_{obs}[C] = [C](k_1[P] + k_2[P]^2)/(1 + k_3[P])$ for the reactions of olefin(tetramethyl-1,4-benzoquinone)nickel complexes with bases (P) [a]

| Temp. | $10^2k_1/M^{-1}\,s^{-1}$ | $10^2k_2/M^{-2}\,s^{-1}$ | $k_3/M^{-1}$ |
|---|---|---|---|
| (A) Olefin = cyclo-octa-1,5-diene, (P) = $Bu_3P$, in heptane | | | |
| $29{\cdot}6_0$° | $0{\cdot}30 \pm 0{\cdot}03$ | (0) [b] | (0) [b] |
| (B) Olefin = cyclo-octa-1,5-diene, (P) = $(MeO)_3P$, in heptane | | | |
| $29{\cdot}6_0$° | $3{\cdot}34 \pm 0{\cdot}36$ | $260 \pm 24$ | $6{\cdot}5 \pm 1{\cdot}4$ |
| $48{\cdot}6_0$ | $15{\cdot}2 \pm 0{\cdot}9$ | $423 \pm 13$ | $3{\cdot}8 \pm 3{\cdot}9$ |
| (C) Olefin = cyclo-octa-1,5-diene, (P) = $(MeO)_3P$, in toluene | | | |
| $29{\cdot}6_0$° | $0{\cdot}35 \pm 0{\cdot}18$ | $36{\cdot}4 \pm 4{\cdot}9$ | $4{\cdot}7 \pm 1{\cdot}0$ |
| $40{\cdot}0_5$ | $1{\cdot}09 \pm 0{\cdot}32$ | $68 \pm 13$ | $4{\cdot}1 \pm 1{\cdot}8$ |
| $49{\cdot}6_0$ | $3{\cdot}53 \pm 0{\cdot}46$ | $107 \pm 27$ | $6{\cdot}0 \pm 2{\cdot}5$ |
| (D) Olefin = cyclo-octa-1,5-diene, (P) = $(BuO)_3P$, in heptane | | | |
| $29{\cdot}6_0$° | $3{\cdot}48 \pm 0{\cdot}16$ | $152 \pm 11$ | $9{\cdot}3 \pm 1{\cdot}1$ |
| (E) Olefin = *endo*-dicyclopentadiene, (P) = $(MeO)_3P$, in toluene | | | |
| $29{\cdot}6_0$° | $24{\cdot}1 \pm 1{\cdot}4$ [c] | (0) [b] | (0) [b] |
| $40{\cdot}0_5$ | $47{\cdot}6 \pm 2{\cdot}3$ [c] | (0) [b] | (0) [b] |
| $49{\cdot}6_0$ | $84{\cdot}4 \pm 2{\cdot}1$ [c] | (0) [b] | (0) [b] |
| (F) Olefin = norborna-2,5-diene, (P) = $(MeO)_3P$, in toluene | | | |
| $29{\cdot}6_0$° | $45{\cdot}2 \pm 1{\cdot}0$ | $750 \pm 90$ | (0) [d] |
| (G) Olefin = cyclo-octatetraene, (P) = $(MeO)_3P$, in toluene | | | |
| $29{\cdot}6_0$° | $19{\cdot}6 \pm 0{\cdot}6$ | $720 \pm 30$ | (0) [d] |
| $40{\cdot}1_0$ | $59{\cdot}5 \pm 1{\cdot}3$ | $500 \pm 90$ | (0) [d] |
| (H) Olefin = tetramethyl-1,4-benzoquinone, (P) = $(MeO)_3P$, in toluene | | | |
| $29{\cdot}6_0$° | $0{\cdot}313 \pm 0{\cdot}004$ [e] | (0) [b] | (0) [c] |
| $40{\cdot}0_5$ | $0{\cdot}840 \pm 0{\cdot}004$ [e] | (0) [b] | (0) [b] |
| $49{\cdot}6_0$ | $1{\cdot}82 \pm 0{\cdot}02$ [e] | (0) [b] | (0) [b] |

[a] Parameters determined by a least mean squares computer programme; errors quoted are standard deviations. [b] For these reactions, results fitted to $k_{obs} = k_0 + k_1[P]$ (see text). Arrhenius parameters from unweighted least squares are: $E_a = 12{\cdot}0 \pm 0{\cdot}1$ kcal, $\Delta S^\ddagger = -23{\cdot}3 \pm 0{\cdot}3$ cal mol$^{-1}$ K$^{-1}$. [d] For these reactions, results fitted to $k_{obs}/[P] = k_1 + k_2[P]$. [e] Arrhenius parameters from unweighted least squares are: $E_a = 16{\cdot}8 \pm 0{\cdot}3$ kcal, $\Delta S^\ddagger = -15{\cdot}4 \pm 1{\cdot}0$ cal mol$^{-1}$ K$^{-1}$.

## DISCUSSION

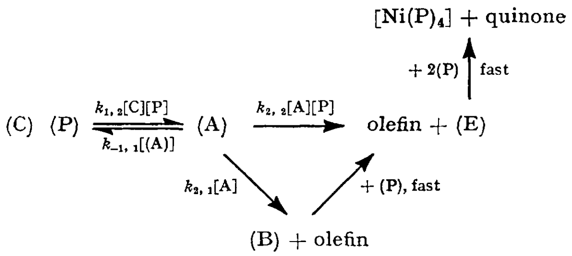
*Reactions of Cyclo-octa-*1,5-*diene*(*tetramethyl*-1,4-*benzoquinone*)*nickel*. Because of the absolute and relative magnitudes of the rate constants involved, our results for this complex give more information than for the other complexes, and we are able to provide good evidence for a fairly detailed mechanism for the reaction of the cyclo-octa-1,5-diene complex with trialkyl phosphites.

In heptane, the cyclo-octa-1,5-diene complex reacts with tributylphosphine to give bis(tributylphosphine)-(tetramethyl-1,4-benzoquinone)nickel which then decomposes slowly, whereas the reactions with tributyl and trimethyl phosphites give tetrakis(phosphite)nickel complexes and no intermediates can be detected from the i.r., u.v., or n.m.r. spectra of the reaction mixtures. The tendency of phosphines to give less complete substitution than phosphites in reactions with low-valent metal complexes is well known,[8] but the result is important here because it shows that the olefin is a better leaving group than the quinone. It is unlikely that the relative ease of displacement of the olefin and quinone changes substantially on change of nucleophile from phosphine to phosphite, so it is probable that the first steps of the reaction of the olefin complex with a phosphite also result in the complete displacement of the olefin ligand.

This conclusion is supported by two other lines of evidence. The complicated form of the rate equation (Table 3) is unlikely to arise from initial displacement of the essentially planar quinone molecule. In the displacement of the rather similar molecules cycloheptatriene and arenes from their (tricarbonyl)-group VI metal derivatives,[6] it appears that the binding of the whole molecule to the metal is weakened as the first nucleophile approaches the metal, which gives a high activation energy to this step and causes the subsequent steps leading to complete displacement of the organic portion to be rapid and not rate determining. We would therefore expect displacement of the quinone always to lead to the rate equation rate $= k[\mathrm{C}][\mathrm{P}]$, and not the form we observe.

If we assume that the rate constant for the reaction of trimethyl phosphite with bis(tetramethyl-1,4-benzoquinone)nickel (Table 3) is that of a rate-determining bimolecular process, displacement of a single quinone molecule is slower by a factor of *ca.* 20 than the reaction of trimethyl phosphite with the cyclo-octa-1,5-diene complex. From the value of $\nu$(CO) for the olefin complex (1553 $\mathrm{cm}^{-1}$) and for the bis(quinone) complex (1580 $\mathrm{cm}^{-1}$) it appears that the quinone may be more strongly bound to nickel in the olefin complex,[4] so displacement of the quinone from the olefin complex would probably be much slower than the reaction we observe.

The equation rate $= k_{\mathrm{obs}}[\mathrm{C}] = [\mathrm{C}](k_1[\mathrm{P}] + k_2[\mathrm{P}]^2)/(1 + k_3[\mathrm{P}])$, gives a good fit to the experimental data for the reaction of trimethyl phosphite in toluene (Figure 1) and equations of this form [Table 4; (A) and (B)] can be derived from the Scheme by applying the stationary-state approximation to the intermediate (A). (For $k_{\mathrm{i,j}}$, i represents the step and direction of reaction, and j its molecularity.)



SCHEME

Intermediate (E) is probably $[\mathrm{Ni(C_{10}H_{12}O_2)(P)_2}]$, and we suggest that (A) is $[\mathrm{Ni(olefin)(C_{10}H_{12}O_2)(P)}]$ in which the olefin is monodentate; (B) is probably co-ordinatively unsaturated $[\mathrm{Ni(C_{10}H_{12}O_2)(P)}]$. The lack of detectable inhibition of the reaction by added diene or quinone [Table 2, footnote (*b*)] supports the view that neither ligand is completely dissociated in (A) and suggests that the reverse of the reactions after step 1 are not significant under our conditions. The nature of the steps leading from (E) to $[\mathrm{Ni\{(MeO)_3P\}_4}]$ is unknown, since they are rapid and do not affect the rate equation. The rate equation is also satisfactory for the reactions of the cyclo-octa-1,5-diene complex with trimethyl phosphite in

TABLE 4

Stationary state equation and limiting forms for mechanism in the Scheme, valid for $k_{1,2}[\mathrm{P}] \ll k_{-1,1} + k_{2,1} + k_{2,2}[\mathrm{P}]$

| | Condition | Extra condition | Expression for $k_{\mathrm{obs}}$ [a] |
|---|---|---|---|
| (A) | $(k_{1,2}[\mathrm{P}] \ll k_{-1,1} + k_{2,1} + k_{2,2}[\mathrm{P}])$ | None | $\dfrac{k_{1,2}k_{2,1}[\mathrm{P}] + k_{1,2}k_{2,2}[\mathrm{P}]^2}{k_{-1,1} + k_{2,1} + k_{2,2}[\mathrm{P}]}$ [b] |
| (B) | $k_{2,1} \ll k_{-1,1} + k_{2,2}[\mathrm{P}]$ | None | $\dfrac{k_{1,2}k_{2,1}[\mathrm{P}] + k_{1,2}k_{2,2}[\mathrm{P}]^2}{k_{-1,1} + k_{2,2}[\mathrm{P}]}$ [b] |
| (C) | | $k_{2,2}[\mathrm{P}] \ll k_{2,1}$ | $\dfrac{k_{1,2}k_{2,1}[\mathrm{P}]}{k_{-1,1}}$ |
| (D) | $k_{2,2}[\mathrm{P}] \ll k_{-1,1} + k_{2,1}$ | None | $\dfrac{k_{1,2}k_{2,1}[\mathrm{P}]}{k_{-1,1} + k_{2,1}} + \dfrac{k_{1,2}k_{2,2}[\mathrm{P}]^2}{k_{-1,1} + k_{2,1}}$ |
| (E) | | $k_{2,1} \ll k_{-1,1}$ | $\dfrac{k_{1,2}k_{2,1}[\mathrm{P}]}{k_{-1,1}} + \dfrac{k_{1,2}k_{2,2}[\mathrm{P}]^2}{k_{-1,1}}$ |
| (F) | $k_{2,2}[\mathrm{P}] \ll k_{2,1}$ | None | $\dfrac{k_{1,2}k_{2,1}[\mathrm{P}]}{k_{-1,1} + k_{2,1}}$ |
| (G) | $k_{2,1} \ll k_{2,2}[\mathrm{P}]$ | None | $\dfrac{k_{1,2}k_{2,2}[\mathrm{P}]^2}{k_{-1,1} + k_{2,2}[\mathrm{P}]}$ |
| (H) | | $k_{2,2}[\mathrm{P}] \ll k_{-1,1}$ | $\dfrac{k_{1,2}k_{2,2}[\mathrm{P}]^2}{k_{-1,1}}$ |
| (I) | $k_{-1,1} \ll k_{2,1} + k_{2,2}[\mathrm{P}]$ | Any | $k_{1,2}[\mathrm{P}]$ |

[a] Under pseudo-first-order conditions with (P) in excess, $k_{\mathrm{obs}}$ is defined by rate $= k_{\mathrm{obs}}[\mathrm{C}]$. [b] An expression with this form of dependence on [P] can be derived for the appearance of products in a mechanism in which a rapid equilibrium which produces intermediate (A) is followed by concurrent unimolecular loss of olefin or bimolecular reaction with (P). The equilibrium constant found by fitting the results for the reaction of the cyclo-octa-1,5-diene complex to this equation is incompatible with the failure to detect intermediates in the u.v. and n.m.r. spectra of reaction mixtures and with the absence of a detectable initial rapid reaction.

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[8] F. Basolo and H. Schuster-Woldan, *J. Amer. Chem. Soc.*, 1966, **88**, 1657; R. F. Heck, *ibid.*, p. 2787.

heptane and tributyl phosphite in heptane. Complexes of other olefins give data which fit rate equations (Table 3) which are not experimentally distinguishable from limiting forms of the complete equation (Table 4).

Although the accuracy of the values of $k_{obs}$ is as high as can be expected, the rate parameters $k_1$—$k_3$ have substantial standard deviations. Since ratios or more complicated functions of these parameters correspond to $k_{1,2}$ or to ratios of other rate constants, the calculation of the primary kinetic constants involves the accumulation of fairly large errors. From the results, it is not possible to check that the stationary state condition $k_{1,2} \ll k_{-1,1} + k_{2,1} + k_{2,2}[P]$, applies in these reactions, but the absence of detectable concentrations of intermediates is consistent with this condition.

TABLE 5

Rate constants for elementary steps in the reactions of olefin(tetramethyl-1,4-benzoquinone)nickel complexes with bases (P) in toluene [a]

| Olefin | (P) | Temp. | $k_{12}/\text{M}^{-1}\ \text{s}^{-1}$ | $(k_{2,2}/k_{2,1})/\text{M}^{-1}$ | $k_{-1,1}/k_{2,1}$ |
|---|---|---|---|---|---|
| Cyclo-octa-1,5-diene | $(MeO)_3P$ | $29{\cdot}6_0$° | $0{\cdot}08 \pm 0{\cdot}02$ | $104 \pm 55$ | $21 \pm 13$ |
| | | $40{\cdot}05$ | $0{\cdot}17 \pm 0{\cdot}08$ | $62 \pm 22$ | $14 \pm 8$ |
| | | $49{\cdot}6_0$ | $0{\cdot}18 \pm 0{\cdot}12$ | $30 \pm 9$ | $4 \pm 5$ |
| | *b* | $29{\cdot}6_0$ | $0{\cdot}4 \pm 0{\cdot}09$ | $78 \pm 11$ [c] | $11 \pm 3$ |
| | *b* | $49{\cdot}6_0$ | $1{\cdot}1 \pm 1{\cdot}1$ | $28 \pm 1$ [c] | [d] |
| | $(BuO)_3P$ [b] | $29{\cdot}6_0$ | $0{\cdot}16 \pm 0{\cdot}02$ | $44 \pm 4$ | $3{\cdot}7 \pm 0{\cdot}5$ |
| Norborna-2,5-diene | $(MeO)_3P$ | $29{\cdot}6_0$ | $>1{\cdot}5$ [e] | $17 \pm 2$ | $>2$ [e] |
| Cyclo-octatetraene | $(MeO)_3P$ | $29{\cdot}6_0$ | $>2{\cdot}2$ [e] | $37 \pm 2$ | $>10$ [e] |
| | | $40{\cdot}1_0$ | [d] | $8{\cdot}4 \pm 1{\cdot}5$ | [d] |
| *endo*-Dicyclopentadiene | $(MeO)_3P$ | See Table 3 | $k_{-1\,1} \ll k_{2,1} + k_{2,2}[P]$ | | |
| Tetramethyl-1,4-benzoquinone | $(MeO)_3P$ | | | | |

[a] Standard deviations ($\sigma$) quoted were obtained for $X = AB^{-1}$ from $(\sigma_X/X)^2 = (\sigma_A/A)^2 + (\sigma_B/B)^2$. [b] Reaction in heptane. [c] $(E_a)_{2,2} - (E_a)_{2,1} = -9{\cdot}9 \pm 3{\cdot}2$ kcal, $\Delta S^\ddagger_{2,2} - \Delta S^\ddagger_{2,1} = -24$ cal mol$^{-1}$ K$^{-1}$. [d] Values have very large standard deviations. [e] Values calculated from an upper limit for $k_3$ (see text). [f] Approximate Arrhenius parameters: $(E_a)_{2,2} - (E_a)_{2,1} = ca.\ -27$ kcal, $\Delta S^\ddagger_{2,2} - \Delta S^\ddagger_{2\,1} = ca.\ -80$ cal mol$^{-1}$ K$^{-1}$.

The reaction between cyclo-octa-1,5-diene(tetramethyl-1,4-benzoquinone)nickel and tributylphosphine is first order in each reactant and the rate parameter is given in Table 3. From Table 4, this parameter could correspond to one of the following expressions: $k_{1,2}k_{2,1}/(k_{-1,1} + k_{2,1})$ (F, $k_{2,2}[P] \ll k_{2,1}$), $k_{1,2}k_{2,1}/k_{-1,1}$ (C, $k_{2,2}[P] \ll k_{2,1} \ll k_{-1,1}$), or $k_{1,2}$ (I, $k_{-1,1} \ll k_{2,1} + k_{2,2}[P]$). The results available do not permit a definite choice to be made, but if $k_1 = k_{1,2}$, the bimolecular rate constant for attack by phosphine ($0{\cdot}3 \times 10^{-2}\text{M}^{-1}\ \text{s}^{-1}$) is smaller than that for trimethyl phosphite ($k_{1,2} = 0{\cdot}4\text{M}^{-1}\ \text{s}^{-1}$) at 30° in heptane. This order of reactivity has not been found in reactions of other metal(0) complexes,[9] which suggests that mechanism (C) or (F) may be operating; for both these cases the rate parameter would be less than $k_{1,2}$, and for case (C) it would be substantially less than $k_{1,2}$.

The reaction of tributylphosphine with cyclo-octa-1,5-diene(tetramethyl-1,4-benzoquinone)nickel (*ca.* $10^{-4}$M) in 1,2-dichloroethane gives a quantitative yield of *cis*-dichlorobis(tributylphosphine)nickel as shown by u.v. spectra, but reactions with larger concentrations of olefin complex give substantial amounts of bis(tributylphosphine)(tetramethyl-1,4-benzoquinone)nickel. Reactions of metal(0) complexes with chlorinated solvents have been used as sources of radicals for polymerisation [10] and have been noted as a complication in the kinetics of displacement reactions,[6] but the metal-containing products have not been identified in such systems. Our investigation of the reaction of the nickel complex is incomplete, but it appears that traces of oxygen or impurities in the solvent are responsible for the production of $[NiCl_2(Bu_3P)_2]$. The kinetics of the reaction were not reproducible even when the conversion was quantitative.

*Reactions of Complexes of Cyclo-octatetraene and Norborna-2,5-diene.*—The results for the complexes of these olefins give graphs of $k_{obs}/[P]$ *vs.* [P] which do not deviate detectably from linearity over the range of trimethyl phosphite concentrations we have been able to study (*e.g.* Figure 2). From these graphs we estimate that in the empirical rate equation [equation (4)] $k_3[P]$ must be less than 0·1 at the highest [P] studied, otherwise curvature would be apparent. This gives upper limits for $k_3$ at 30° as $k_3 < 3{\cdot}3\text{M}^{-1}$ for the cyclo-octatetraene complex and $k_3 < 5\text{M}^{-1}$ for the norborna-2,5-diene complex. The lower limits given for $k_{1,2}$ in Table 5 are then calculated from the relation $k_{1,2} = k_2/k_3$. If the conditions for (D) or (E) of Table 4 are fulfilled, $k_{2,2}/k_{2,1} = k_2/k_1$, but this relation can be used to obtain fairly accurate values of $k_{2,2}/k_{2,1}$ even if the values of $k_3$ are at the upper limits given above. Since $k_3 = k_{2,2}/(k_{-1,1} + k_{2,1})$, a lower limit on the magnitude of $k_{-1,1}$ compared with $k_{2,1}$ can also be obtained (Table 5).

Although an explanation based on Table 5 is the most reasonable, our results do not exclude the possibility that the rate law arises from concurrent unimolecular and bimolecular reactions of the olefin complexes.

*Reaction of* endo-*Dicyclopentadiene Complex.*—The kinetics of the reaction with trimethyl phosphite do not deviate appreciably from the equation rate $= k_1[C][P]$, so from Table 5, $k_1$ is given by one of the following expressions: $k_{1,2}k_{2,1}/(k_{-1,1} + k_{2,1})$, (F, $k_{2,2}[P] \ll k_{2,1}$); $k_{1,2}k_{2,1}/k_{-1,1}$ (C, $k_{2,2}[P] \ll k_{2,1} \ll k_{-1,1}$); $k_{1,2}$ (I, $k_{-1,1} \ll k_{2,1} + k_{2,2}[P]$); ($k_{1,2}$ is the rate constant for the

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[9] R. J. Angelici, *Organometallic Chem. Rev.*, 1968, **3A**, 173.

[10] C. H. Bamford and C. A. Finch, *Trans. Faraday Soc.*, 1963, **59**, 118.

rate-determining step). An additional possibility is that two rate constants $k_{1.2}{}^{a}$ and $k_{1.2}{}^{b}$ are involved, which correspond to displacement of the nonequivalent donor groups of the *endo*-dicyclopentadiene ligand. However, this and case (F) probably do not apply, because a linear plot of log $k_1$ *vs* $1/T$ was obtained from the results in Table 3 [see footnote (*c*)]. In compounds containing *endo*-dicyclopentadiene linked to a transition metal by only one bond, the metal is bonded to the carbon–carbon double bond of the bicycloheptene ring,[11] which suggests that the bond from nickel to the five-membered ring is broken in the initial step of the present system.

Although the entropy of activation $\Delta S^{\ddagger}$ [$-23{\cdot}3 \pm 0{\cdot}3$ cal mol$^{-1}$ K$^{-1}$ Table 3, footnote (*c*)], is appropriate for a bimolecular reaction implied by $k_{1.2}$ [case (I), Table 4] this could represent the overall entropy of activation for case (C), but comparison of $k_1$ with the value of $k_{1.2}$ for cyclo-octa-1,5-diene leads us to prefer case (I) at present. Thus, if this is correct, the results imply that the $S_N2$ reaction of the *endo*-dicyclopentadiene complex is a factor of *ca.* 6 times faster than for the cyclo-octa-1,5-diene complex, and this ratio seems reasonable. If case (C) is operative, however, since this equation is derived under the condition $k_{2.1} \ll k_{-1.1}$, it follows that $k_{1.2} \gg k_1$ and this implies a large difference in the reactivities of the *endo*-dicyclopentadiene and cyclo-octa-1,5-diene complexes. Experiments to determine the relative reactivity of other complexes of these olefins are in progress.[12]

*Reaction of Bis(tetramethyl-*1,4*-benzoquinone)nickel.*—In common with several other systems in which an uncharged planar organic molecule (or a planar part of a molecule) is displaced from a metal,[6,13] the kinetics are of the form rate $= k_1$[C][P], and the entropy of activation is appropriate for an $S_N2$ process [Table 4, footnote (*e*)]. As noted earlier, the first step is probably rate determining, because the binding of the whole molecule to the metal is weakened and this facilitates the subsequent steps. The condition for a rate-determining initial step in terms of the Scheme is that $k_{-1.1} \ll k_{2.1} + k_{2.2}$[P] and it seems probable that $k_{-1.1}$ may well be much smaller for such poor nucleophiles as arenes than for ligands with separated double bonds such as cyclo-octa-1,5-diene.

*Rate Constants for Elementary Steps.*—The results for reactions with trimethyl phosphite in toluene at 30° give rate constants $k_{1.2}$ for the initial $S_N2$ processes which increase in the order: tetramethyl-1,4-benzoquinone $\ll$ cyclo-octa-1,5-diene $<$ *endo*-dicyclopentadiene $<$ norborna-2,5-diene or cyclo-octatetraene. This order of lability is qualitatively similar to the order of stability determined by ligand-exchange studies:[14] cyclo-octa-1,5-diene $>$ *endo*-dicyclopentadiene $>$ norborna-2,5-diene $>$ cyclo-octatetraene. Because the dependence of $k_{\text{obs}}$ on [P] is different for the different olefins, relative rates of displacement at a particular phosphite concentration cannot be used as a guide to the relative ease of the $S_N2$ reactions. It is probable that the reactivity order towards dimethylglyoxime, reported by Schrauzer,[14] differs in this respect. Even a full kinetic analysis over a reasonably wide range of phosphite concentrations fails to give more than a lower limit for $k_{1.2}$ for two of the olefins.

The results are of sufficient accuracy to show that $k_{2.2}/k_{2.1}$ decreases with increasing temperature for the cyclo-octa-1,5-diene and cyclo-octatetraene complexes, but for $k_{-1.1}/k_{2.1}$, where the temperature dependence may be rather small, the errors are too large for a trend to be apparent. For the cyclo-octa-1,5-diene complex the values of $(E_a)_{2.2} - (E_a)_{2.1}$ and $\Delta S^{\ddagger}{}_{2.2} - \Delta S^{\ddagger}{}_{2.1}$ [Table 5, footnote (*c*)] appear reasonable and for the cyclo-octatetraene complex, where $\Delta S^{\ddagger}{}_{2.2} - \Delta S^{\ddagger}{}_{2.1}$ is large and negative, the result is based on only four values of $k_{\text{obs}}$ at $40{\cdot}1_0$°.

For the cyclo-octa-1,5-diene complex the rate parameters $k_1$ and $k_2$ are larger for the reaction in heptane than in toluene; this is mainly due to $k_{1.2}$ being larger in heptane than toluene.

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