Reactivity of Cyanogen with Monocarbonylnickel(0) Complexes. Examples of Combined Oxidative Substitution and Internal Ligand Substitution

By **Benedetto Corain,* Marino Basato,** and **Giancarlo Favero,** Centro di Studio sulla Stabilità e Reattività dei Composti di Coordinazione, C.N.R., Istituto di Chimica Analitica, University of Padova, 35100 Padua, Italy

The complex [Ni(CO)(dppb)$_2$] (dppb = Ph$_2$P[CH$_2$]$_4$PPh$_2$) undergoes a two-stage reaction with C$_2$N$_2$ in CH$_2$Cl$_2$, at room temperature. The first stage gives almost equivalent quantities of [{Ni(CN)$_2$(dppb)}$_2$] and [Ni(CO)$_2$(dppb)], whereas quantitative conversion of [Ni(CO)$_2$(dppb)] into [{Ni(CN)$_2$(dppb)}$_2$] and CO is obtained in the second stage. The complexes [Ni(CO)(dppb){P(OR)$_3$}] (R = Et or Ph) react in a similar way under particular conditions. A kinetic investigation has been carried out on the first system and a reaction mechanism is proposed for its first stage.

CYANOGEN is a molecule of potential interest in organic synthesis. Organic reactions involving the breaking of the very strong carbon–carbon bond (dissociation energy 132 ± 6 kcal mol^{-1}) [1,†] are very rare,[2] and the technologically interesting reaction of C$_2$N$_2$ with the olefinic double bond to give saturated nitriles is almost unknown. The latter reaction can be carried out at high temperatures over metallic nickel and chromium catalysts and by electric discharge,[2,3] giving low yields.

The co-ordination of cyanogen appears to be rather interesting as the molecule is known to behave as a ligand towards Mn^0,[4] Rh^{I},[5] Rh^{III},[6] and Ru^{II} and Ru^{III},[7] and as an oxidant towards Ni^0, Pd^0, Pt^0, and Rh^{I}.[5] In view of the recognized ability of some nickel(0) complexes to catalyze the addition of HCN to olefins,[8] we report here on the reactions of C$_2$N$_2$ with monocarbonyl complexes of Ni^0, in particular four-co-ordinate [Ni(CO)(dppb)$_2$] [1; dppb = 1,4-bis(diphenylphosphino)butane].[9]

EXPERIMENTAL

All the operations concerning the nickel(0) complexes were conducted under argon.

Materials.—The solvent was quality-grade dichloromethane (C. Erba) which was used as received. Complex (1) was prepared according to ref. 9. Cyanogen was from Baker. Standard cyanogen solutions were prepared by condensing the gas from the cylinder into dichloromethane cooled at −80 °C. The cyanogen concentration was determined from the absorbance of the ν_{asym}(CN) band at 2 150 cm^{-1} according to ref. 10. 1,4-Bis(diphenylphosphino)butane was prepared according to ref. 11.

Instruments.—Infrared analysis was carried out on a Perkin-Elmer 257 instrument equipped with permanent NaCl cells of suitable pathlength; wavenumbers are accurate to ±2 cm^{-1} at *ca*. 2 000 cm^{-1}. Carbon monoxide analysis was carried out on a Hewlett–Packard 5750 gas chromatograph with a 2-m column of molecular sieves. Spectra in the visible region were recorded on an Optica CF4 instrument.

Procedures.—(*i*) *The reaction between* (1) *and* C$_2$N$_2$. The reaction was followed by monitoring the i.r. spectra of the reacting solutions, the initial concentrations of the reagents being 1.25×10^{-3}—1×10^{-2} mol dm^{-3} Ni^0 and 1.7×10^{-2}—4.7×10^{-1} mol dm^{-3} C$_2$N$_2$. In a few cases the reaction was also studied in the presence of dppb (5×10^{-2}—5.2×10^{-1} mol dm^{-3}) or CO (*ca*. 2.5×10^{-4}—*ca*. 5×10^{-3} mol dm^{-3}). Kinetic runs were carried out in three-necked flasks (*ca*. 50 cm^3) thermostatted at 21 ± 0.1 °C. At various times, aliquot portions of the reacting solution were removed from the reaction vessel through a rubber cap by means of a stainless-steel syringe. The disappearance of (1) was monitored at 1 907 cm^{-1} [ν(CO)]. The volume of the CH$_2$Cl$_2$ solutions was typically 10 cm^3 and the reaction mixture was maintained under vigorous stirring.

The reaction products were identified on the basis of their characteristic ν(CN) and ν(CO) bands {2 115 cm^{-1} for *trans*-[{Ni(CN)$_2$(dppb)}$_2$], 2 100 cm^{-1} for the moiety *trans*-Ni(CN)$_2$(dppb)$_2$, and 1 935 and 1 995 cm^{-1} for [Ni(CO)$_2$(dppb)]}.[9,11] The concentration of the moiety Ni(CN)$_2$(dppb) was determined as described elsewhere,[12] and that of [Ni(CO)$_2$(dppb)] was estimated as reported in ref. 10. Carbon monoxide analysis during the first stage of reaction was carried out by taking six samples (0.5 cm^3) of the gas in equilibrium with the reacting solutions at various times by means of a gas-tight syringe. The resulting g.c. peak areas were compared with that of a standard mixture (1% CO in argon) in equilibrium with CH$_2$Cl$_2$ (10 cm^3) contained in a vessel identical to that employed for the kinetic runs. Carbon monoxide analysis at the end of the reaction was carried out in a similar way.

(*ii*) *The reaction of* [Ni(CO)(dppb){P(OPh)$_3$}] *and* [Ni(CO)(dppb){P(OEt)$_3$}] *and* C$_2$N$_2$. The reacting complexes were generated *in situ* as described in ref. 13 using a ligand : nickel mol ratio of 1 : 1. Apparatus and general conditions were identical to those described for the reaction of (1). The

---

[†] Throughout this paper: 1 cal = 4.184 J; 1 atm = 101 325 Pa.

[1] Gmelin's 'Handbuch der Anorganischen Chemie,' Verlag Chemie, 1971, vol. 14, Teil D1, p. 54.

[2] T. K. Brotherton and J. W. Lynn, *Chem. Rev.*, 1959, **59**, 841.

[3] T. Isshiki, N. Sonoda, and S. Tsutsumi, *Bull. Chem. Soc. Japan*, 1969, **41**, 2180.

[4] J. F. Guttenberger, *Angew. Chem. Internat. Edn.*, 1967, **6**, 1081.

[5] M. Bressan, G. Favero, B. Corain, and A. Turco, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 203.

[6] G. Favero, B. Corain, P. Rigo, and A. Turco, *Gazzetta*, 1973, **103**, 297.

[7] G. M. Tom and H. Taube, *J. Amer. Chem. Soc.*, 1975, **97**, 5310.

[8] B. W. Taylor and H. E. Swift, *J. Catalysis*, 1972, **26**, 254 and refs. therein.

[9] B. Corain, M. Bressan, and G. Favero, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 197.

[10] B. Corain, G. Favero, and A. Minciullo, *Gazzetta*, 1976, **106**, 671.

[11] P. Rigo, B. Corain, and A. Turco, *Inorg. Chem.*, 1968, **7**, 1623.

[12] B. Corain, P. Rigo, and G. Favero, *Inorg. Chem.*, 1971, **10**, 2329.

[13] B. Corain and L. De Nardo, *J. Organometallic Chem.*, 1976, **110**, C27; B. Corain, L. De Nardo, and G. Favero, *ibid.*, 1977, **125**, 105.

reactions were followed according to two different methods. (*a*) The reaction mixture was prepared in the usual vessel. As soon as possible the solution was transferred into an i.r. cell thermostatted at 21 ± 0.2 °C inside an air-controlled thermostat and the i.r. spectrum was occasionally monitored (conditions hereafter referred to as the 'closed system'). (*b*) Infrared analysis was carried out exactly as described for (1) ('open system'). Only for [Ni(CO)(dppb){P(OEt)$_3$}] was the reaction with C_2N_2 carried out in a stainless-steel autoclave (100 cm^3) at p_{CO} = 3 atm.

RESULTS AND DISCUSSION

Spectrophotometric Analysis of the System [Ni(CO)L$_3$]–C_2N_2.—Complex (1) reacts with cyanogen according to equations (1) and (2). For $[Ni]_0 = 10^{-2}$ mol dm^{-3} and $[C_2N_2] = 0.1$ mol dm^{-3} the first stage lasts *ca.* 20 min

$$2[\mathrm{Ni(CO)(dppb)_2}] + \mathrm{C_2N_2} \xrightarrow{\text{stage I}} 0.5[\{\mathrm{Ni(CN)_2(dppb)}\}_2] + [\mathrm{Ni(CO)_2(dppb)}] + 2\mathrm{dppb} \quad (1)$$

$$[\mathrm{Ni(CO)_2(dppb)}] + \mathrm{C_2N_2} \xrightarrow{\text{stage II}} 0.5[\{\mathrm{Ni(CN)_2(dppb)}\}_2] + 2\mathrm{CO} \quad (2)$$

and the second requires *ca.* 24 h to go to completion. The first stage produces 0.28 mol (±0.01, average from six independent measurements) of the well known [10,11] *trans*-dicyano-complex [{Ni(CN)$_2$(dppb)}$_2$] * per mol of (1) and *ca.* 0.4 mol of [Ni(CO)$_2$(dppb)]. G.c. analysis shows the presence of trace amounts of CO [*ca.* 0.02 mol per mol of (1)] at the end of the first stage. G.c. and spectrophotometric analyses at the end of the second stage gave in a typical experiment ($[Ni^0]_0 = 10^{-2}$ mol dm^{-3}) the following figures: $[Ni^{II}] = 0.98 \times 10^{-2}$ mol dm^{-3} (calculated as monomeric species); CO = *ca.* 0.9 mol per mol of (1).

Some spectra recorded during the reaction are collected in Figure 1. It is worthwhile to point out that the spectral pattern does not depend at all on whether the 'closed' or 'open' systems was used (see Experimental section). The first stage of reaction appears to be a combination of oxidative addition and internal ligand substitution and, as far as we know, this is uncommon in co-ordination chemistry, perhaps unique. The second stage is a fairly common oxidative substitution and cyanogen behaves as an ordinary oxidative-addition reagent.

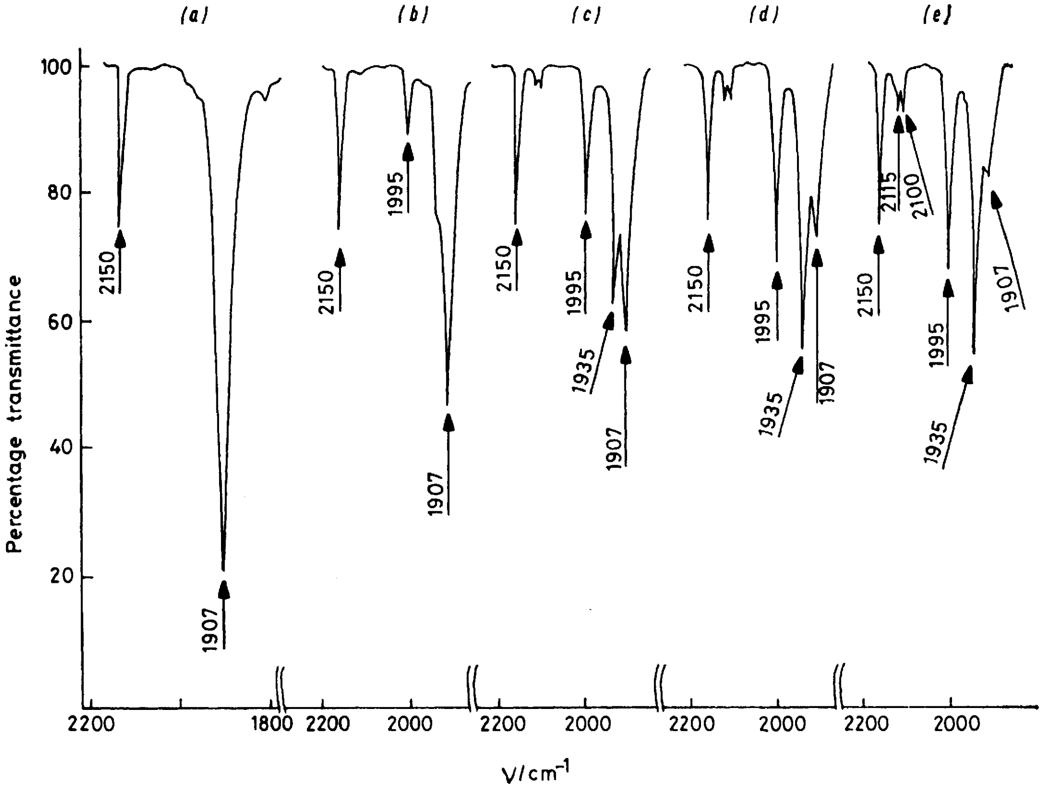


FIGURE 1 Infrared spectra recorded during the reaction between [Ni(CO)(dppb)$_2$] and C_2N_2 at $[Ni^0] = 10^{-2}$ mol dm^{-3}, $[C_2N_2] = 2.5 \times 10^{-1}$ mol dm^{-3}, cell path = 0.5 mm, and 21 ± 0.1 °C after 0 (*a*), 2 (*b*), 5 (*c*), 9 (*d*), and 13 min (*e*)

The complexes [Ni(CO)(dppb){P(OPh)$_3$}] and [Ni(CO)(dppb){P(OEt)$_3$}] behave similarly to (1) under the same concentration conditions provided the reactions are followed in a 'closed' system or under a moderate CO pressure. In the 'open' system both complexes undergo direct oxidative substitution to give air-stable cyano-

---

* Because of the release of dppb during stage I the dimeric complex [{Ni(CN)$_2$(dppb)}$_2$] undergoes a fast equilibrium reaction with dppb to give the five-co-ordinate complex [{Ni(CN)$_2$(dppb)$_2$}$_2$],[11] in which one dppb molecule per nickel atom acts as a unidentate ligand. This latter complex is responsible for the i.r. peak at 2 100 cm^{-1} (Figure 1).

complexes absorbing at 2 110 cm^{-1} and free CO. On the basis of the i.r. data and of the known bridging ability of the dppb ligand,[11] we tentatively propose that these species are the four-co-ordinate dimeric square-planar complexes *trans*-[$Ni_2(CN)_4(dppb)\{P(OR)_3\}_2$] in which one dppb molecule joins two $Ni(CN)_2\{P(OR)_3\}$ moieties. In the ' closed ' system the reaction produces [$Ni(CO)_2(dppb)$] and cyano-complexes absorbing at 2 110 and 2 100 cm^{-1}. The band at 2 100 cm^{-1} is tentatively attributed to the dimeric five-co-ordinate complexes [$Ni_2(CN)_4(dppb)\{P(OR)_3\}_4$] in which one dppb molecule joins two $Ni(CN)_2\{P(OR)_3\}_2$ moieties. The formation of such five-co-ordinate species is a consequence of the change in the overall stoicheiometry of the reactions, which implies the release of free phosphite from the co-ordination sphere of nickel and the consequent opportunity for its co-ordination to the moiety $Ni(CN)_2(dppb)_{0.5}\{P(OR)_3\}$ [ν(CN) at 2 110 cm^{-1}].[14]

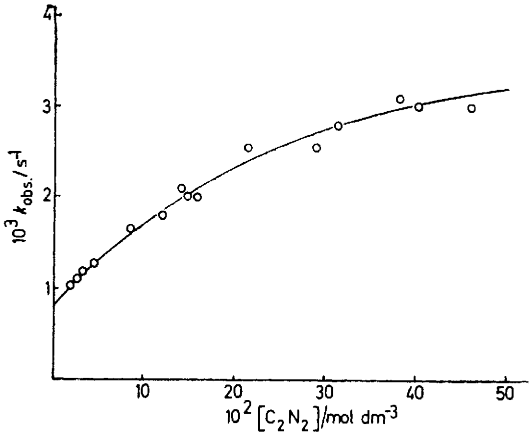
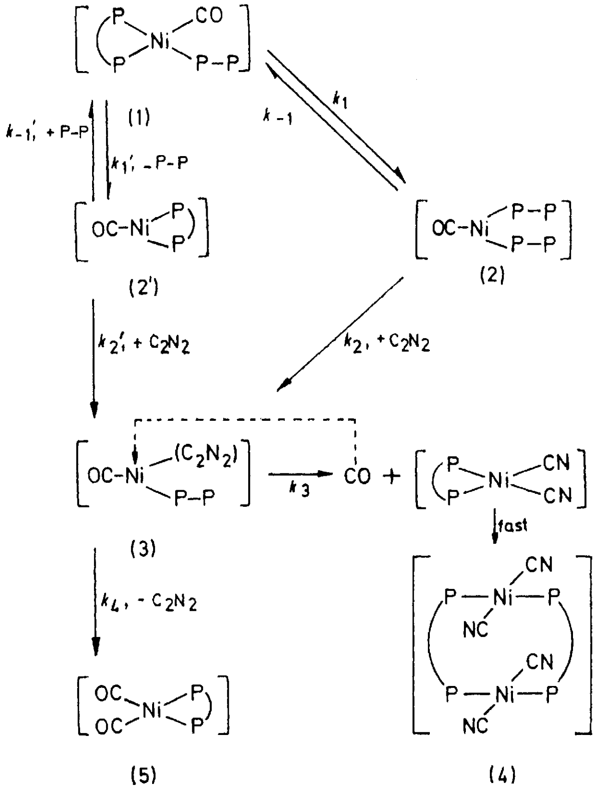


FIGURE 2 Dependence of $k_{obs.}$ on C_2N_2 concentration for the first stage of the reaction of [$Ni(CO)(dppb)_2$] with C_2N_2 in the absence of added dppb and CO

It can be concluded that the reaction of cyanogen with the complexes [$Ni(CO)L_3$] is a combination of oxidative substitution and internal ligand substitution in all cases for (1), but only under forced conditions (*i.e.* in a ' closed ' system in which CO is not allowed to leave the liquid phase) for [$Ni(CO)(dppb)\{P(OPh)_3\}$] and [$Ni(CO)(dppb)\{P(OEt)_3\}$].

Kinetics of the Reaction between [$Ni(CO)(dppb)_2$] *and* C_2N_2.—Only the kinetics of the first stage were studied. The reaction was monitored by following the decreasing absorbance of the peak at 1 907 cm^{-1} of the starting complex ($[Ni^0]_0 = 1.25 \times 10^{-3}$—$1 \times 10^{-2}$ mol dm^{-3}). Under pseudo-first-order conditions plots of $\log|A_t - A_\infty|$ against time were linear over three half-lives. Fifteen different C_2N_2 concentrations were used to investigate the dependence of $k_{obs.}$ on $[C_2N_2]$. Kinetic data are summarized in Figure 2, which shows a curve with a finite intercept when $[C_2N_2] = 0$. The dependence of $k_{obs.}$ on $[C_2N_2]$, in the absence of added CO and/or dppb, takes the form $k_{obs.} = a + \{b/(1 + c[C_2N_2]^{-1})\}$. The kinetic data, as well as the relative quantities of products, are consistent with the following mechanism where $k_1 = 3.3 \times 10^{-3}$ s^{-1}, $k_1' = 0.82 \times 10^{-3}$ s^{-1}, $k_2/k_{-1} = 3.5$ dm^3 mol^{-1}, and $k_2'/k_{-1}' = ca.$ 20.



If we consider species (2), (2′), and (3) as very reactive intermediates, the observed rate of disappearance of (1) takes the form (3) which in the absence of added dppb,

$$k_{obs.} = k_{obs.1} + k_{obs.2} = \frac{k_1 k_2[C_2N_2]}{k_{-1} + k_2[C_2N_2]} + \frac{k_1' k_2'[C_2N_2]}{k_{-1}'[dppb] + k_2'[C_2N_2]} \quad (3)$$

when $k_{-1}'[dppb] \ll k_2'[C_2N_2]$, reduces to the form found experimentally. In this case equation (3) can be rearranged to $1/(k_{obs.} - k_1') = (1/k_1) + (k_{-1}/k_1 k_2[C_2N_2])$ so that a linear dependence of $1/(k_{obs.} - k_1')$ on $1/[C_2N_2]$ is expected. A good linear plot (Figure 3), with intercept $1/k_1$ and gradient $k_{-1}/k_1 k_2$, was indeed obtained by assuming for k_1' the graphically extrapolated value of 0.82×10^{-3} s^{-1}.

The above mechanism also predicts an almost equivalent formation of (4) and (5) with final [CO] = 0, if it is assumed that the rate of formation of (5) by reaction of (3) with CO is almost equal to the rate of production of CO [together with (4)], or, in other words, that $k_4[CO] = k_3$. A consequence of this assumption is that addition of CO should have no effect on the observed rate of disappearance of (1), but a drastic effect on the relative quantities of (4) and (5), because of the higher

---

[14] E. J. Lukosius and K. J. Coskran, *Inorg. Chem.*, 1975, **14**, 1922.

rate of CO attack on (3) to give (5) compared with the rate of intramolecular rearrangement of (3) to give (4).

Two runs were performed at $[C_2N_2] = 0.2$ mol dm^{-3}, without added CO and with constant p_{CO} *ca.* 5×10^{-2} atm (*ca.* 2.5×10^{-4} mol dm^{-3} in solution).[15] The ratio of $[(5)] : [(4)]$ changes as expected in favour of (5) from *ca.* 1 to *ca.* 4 : 1, whereas $k_{obs.}$ becomes *ca.* 20% higher, changing from 2.07×10^{-3} to 2.50×10^{-3} s^{-1}. This difference in $k_{obs.}$ may be attributable to direct attack by CO on the intermediates (2) and (2′) caused by the higher CO concentration in the last case. In order to check this possibility the 'simple' reaction of (1) with CO to give (5) was studied. With $p_{CO} = 1$ atm (*ca.* 10^{-3} mol dm^{-3} in solution),[15] the observed pseudo-first-order rate constant for disappearance of (1) is equal to 1.60×10^{-3} s^{-1}. This value is lower than that observed at p_{CO} *ca.* 5×10^{-2} atm in the presence of $[C_2N_2] = 0.2$ mol dm^{-3} and this clearly indicates that the presence of C_2N_2 increases the rate of carbonylation of (1) in that it produces the reactive intermediate (3) which is much more susceptible to CO attack than are (2) and (2′). Furthermore, it can be shown that the observed 20% increase in $k_{obs.}$ can be roughly accounted for if it is assumed that carbonylation in the absence of C_2N_2 goes *only* through the intermediates (2) and (2′).

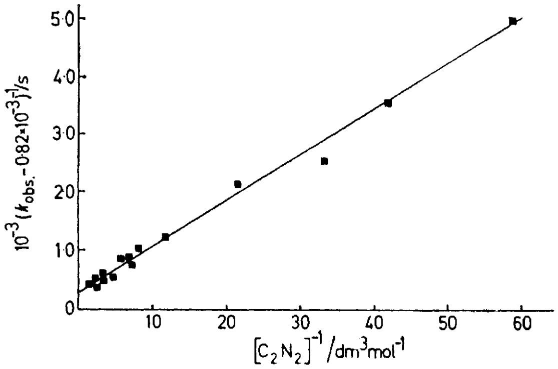


FIGURE 3 Linear dependence of $1/(k_{obs.} - 0.82 \times 10^{-3})$ on $1/[C_2N_2]$ for the data of Figure 2

Some experiments were also carried out to check the effect of free dppb on the rate of the reaction at $[(1)] = 1.25 \times 10^{-3}$, $[C_2N_2] = 3.0 \times 10^{-2}$, and $[\text{dppb}] = 5 \times 10^{-2}$, 28.2×10^{-2}, and 52×10^{-2} mol dm^{-3}. The presence of added dppb has a dramatic effect on the spectral pattern previously described (Figure 1). In particular *no* $[Ni(CO)_2(dppb)]$ *or other carbonyl complexes* are formed in solution and the reaction gives directly $[\{Ni(CN)_2(dppb)\}_2]$ in equilibrium with its five-co-ordinate partner.[11] This finding is in agreement with the reaction mechanism proposed, in that it can be reasonably stated that excess of dppb can block the fourth co-ordination site of (3) preventing CO attack and therefore the formation of (5). Kinetic experiments have shown that the observed pseudo-first-order constant for disappearance of (1) decreases slightly as the dppb concentration increases. The three $k_{obs.}$ values obtained (1.1×10^{-3}, 9.3×10^{-4}, and 9.0×10^{-4} s^{-1}, compared with 1.18×10^{-3} s^{-1} without added dppb) confirm that dppb has little effect on the reaction rate, as expected from the good linearity of the first-order rate plots in the absence of added dppb. Furthermore, these values allow us to estimate a value of *ca.* 20 for the competition quotient k_2'/k_{-1}', *i.e.* the ratio of the rates of bimolecular attack on (2′) by C_2N_2 and dppb. This value is consistent with those normally found for bimolecular attack on unhindered intermediates, these figures being normally close to unity.[16] Also it can be compared with the value of 3.5 dm^3 mol^{-1} found for k_2/k_{-1} where the competition is between attack of C_2N_2 and the free arm of unidentate dppb on the intermediate (2). It is reasonable to assume that entropic factors are here responsible for a relatively more favoured attack by the phosphorus atom of the bonded compared with the 'free' dppb.

A final comment seems necessary on the mechanism in which it is proposed that CO discriminates sharply between (2) [and (2′)] and (3) to give (5). Both (2) [and (2′)] and (3) are three-co-ordinate highly reactive intermediates but the co-ordination of C_2N_2 would strongly favour attack of CO on Ni^0. This statement appears reasonable on considering that an *N*-bonded C_2N_2 can be electronically compared with *N*-bonded saturated nitriles,[6] which implies a better σ-donor ability of C_2N_2 [in (3)] than that of the co-ordinated arm of dppb in (2) and (2′).

We thank Mr. A. Ravazzolo for accurate technical assistance.

[6/1511 *Received, 3rd August,* 1976]

---

[15] 'International Critical Tables,' McGraw-Hill Book Company, 1928, vol. 3, p. 255.

[16] M. Basato, *J.C.S. Dalton*, 1976, 1678 and refs. therein.