Kinetics and Mechanism of the Oxidative Addition of Cyanogen to $[Ni(CO)_2(PPh_3)_2]$ †

Marino Basato,* Benedetto Corain, Giancarlo Favero,* and Pietro Rosano
Centro di Studio sulla Stabilita' e Reattivita' dei Composti di Coordinazione, C.N.R., Istituto di Chimica Analitica, University of Padova, via Marzolo 1, 35100 Padova, Italy

The complex $[Ni(CO)_2(PPh_3)_2]$, (1), reacts with C_2N_2 in toluene, at 30.0—44.5 °C, to give *trans*-$[Ni(CN)_2(PPh_3)_2]$, (2), which crystallizes as a clathrate containing 1 mol of C_2N_2. The reaction mechanism postulated involves preliminary carbon monoxide dissociation from complex (1), followed by competitive cyanogen attack on the three-co-ordinate $[Ni(CO)(PPh_3)_2]$ intermediate and subsequent oxidative addition.

Cyanogen (ethanedinitrile) addition to organic compounds can be achieved under drastic conditions without any selectivity control.[1,2] On the contrary, highly selective quantitative cyanation of a variety of β-dicarbonyl compounds occurs at ambient conditions in the presence of catalytic amounts of $[M(acac)_n]$ ($M = Ni^{II}$, Cu^{II}, Zn^{II}, Co^{II}, Mn^{II}, or Mn^{III}; acac = acetylacetonate) complexes.[3] Cyanogen is also activated by low-valent metal complexes, giving either 'nitrile-like' co-ordination to the metal or oxidative addition with fission of the C–C bond.[3]

We are particularly interested in this last reaction in that it should represent the crucial step of the so far unknown metal-catalysed synthesis of saturated nitriles from cyanogen and olefins. We report here a mechanistic study on the reaction of C_2N_2 with $[Ni(CO)_2(PPh_3)_2]$ in toluene in the temperature range 30.0—44.5 °C.

Experimental

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

Materials.—The solvent toluene (J. T. Baker analysed) was refluxed for 24 h over Na–K and then distilled under inert gas in a flask containing activated molecular sieves. Cyanogen was from Matheson or Schuchard. Triphenylphosphine (J. T. Baker) was recrystallized from CH_2Cl_2–CH_3OH. Carbon monoxide and nitrogen were high-purity (>99.9%) SIO products. Certified Ar–CO mixtures were provided by SIAD, relative errors in their analysed contents being always less than 0.5%.

The complex $[Ni(CO)_2(PPh_3)_2]$, (1), was a Ventron GMBH product used as received. The complex $[Ni(CN)_2(PPh_3)_2]\cdot C_2N_2$ was prepared by reaction of (1) (0.20 g, 0.31 mol) with C_2N_2 (10 cm³ of a 0.83 mol dm⁻³ solution in toluene, 8.3 mmol). After 7 d the product was filtered off and washed with n-hexane, yield 80% (Found: C, 69.7; H, 4.35; N, 8.15. Calc. for $C_{40}H_{30}N_4NiP_2$: C, 69.9; H, 4.40; N, 8.15%). A full characterization including the *X*-ray structure, of this compound has been published elsewhere.[4]

Procedure.—A three-necked flask (50 cm³) containing a weighed quantity of complex (1) and, if required, of PPh_3 was connected to a vacuum line of volume *ca.* 500 cm³. Both the flask and vacuum line were filled with the appropriate gas (Ar, Ar–CO mixture, or CO) by three pump–thaw cycles. A standardized C_2N_2 solution (5 cm³) was added to the flask with a syringe, through a rubber cap, and the solution vigorously stirred. The total pressure in the system was 1.02 atm. The positive pressure facilitated withdrawal *via* a syringe of aliquot portions of the reacting solution for i.r. monitoring; the large volume of the apparatus (*ca.* 550 cm³) minimized changes in the CO partial pressure (when an Ar–CO mixture was used) due to CO release during the reaction.

Determination of C_2N_2 *and* CO *Concentrations.*—Standard cyanogen solutions were prepared by condensing the gas from a cylinder into toluene at −80 °C. The cyanogen concentration was determined from the absorbance of the $\nu_{asym}(CN)$ band at 2 150 cm⁻¹ according to ref. 5 and was shown to be constant during each kinetic run. The molar concentration of CO was calculated from literature data,[6] neglecting the cyanogen vapour pressure.

Instruments.—Aliquot portions of the reacting solutions were monitored in the CO stretching region with a Perkin-Elmer 599B spectrophotometer, using 0.093-mm NaCl cells, the reference containing PPh_3 as appropriate.

Results and Discussion

Reaction of $[Ni(CO)_2(PPh_3)_2]$, (1), with C_2N_2 in toluene always gives quantitative formation of $[Ni(CN)_2(PPh_3)_2]$, (2), which crystallizes as a clathrate containing 1 mol of C_2N_2 per mol of complex [equation (i)]. The course of the reaction is, however,

$$[Ni(CO)_2(PPh_3)_2] + C_2N_2 \longrightarrow [Ni(CN)_2(PPh_3)_2] + 2CO \quad (i)$$

markedly dependent on the experimental conditions adopted.

Reaction (i) *under* Ar.—An appreciable accumulation of $[Ni(CO)_3(PPh_3)]$[7] [ν(CO) at *ca.* 2 050 cm⁻¹] is observed as a consequence of substitution of PPh_3 in complex (1) by released CO. Addition of PPh_3 ($\geqslant 5.0 \times 10^{-2}$ mol dm⁻³) and vigorous stirring minimizes this accumulation, leading to a smooth transformation of complex (1) into (2), as indicated by the disappearance of the ν(CO) bands of (1) at 1 980 and 1 940 cm⁻¹ and the parallel growth of the band of (2) at 2 120 cm⁻¹. Under pseudo-first-order conditions, $[C_2N_2]/[(1)] \geqslant 20$, plots of log A_t *vs.* time (A_t = absorbance of the peak at 1 980 cm⁻¹ at various times) are linear only for *ca.* 1 half-life, thus making inaccurate a definite evaluation of the reaction order. However, the independence of the initial $k_{obs.}$ values (Table 1) on the PPh_3 concentration clearly indicates that PPh_3 has no effect on the reaction rate.

Reaction (i) *under* CO.—In the presence of 1 atm CO an almost quantitative formation of $[Ni(CO)_3(PPh_3)]$ is observed after *ca.* 3 h. Also, in this case, addition of PPh_3 reduces the

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† *Non-S.I. unit employed:* atm = 101 325 Pa.

Table 1. Kinetic data for the reaction $[Ni(CO)_2(PPh_3)_2] + C_2N_2 \longrightarrow [Ni(CN)_2(PPh_3)_2] + 2CO$ in toluene. $[Ni]_0 = 7.5 \times 10^{-3}$ mol dm^{-3}

$\frac{\theta_c}{°C}$	$10^3[C_2N_2]$	$10^3[PPh_3]$	y_{CO} [a]	$10^3[CO]$	$10^5k_{obs.}$
	mol dm^{-3}			mol dm^{-3}	s^{-1}
30.0	800	50.0	0.000	0.000	4.5 [b]
	800	75.0	0.000	0.000	4.5 [b]
	800	100	0.000	0.000	4.8 [b]
	800	125	0.000	0.000	4.1 [b]
	800	150	0.000	0.000	4.1 [b]
	800	200	0.000	0.000	4.4 [b]
	800	450	0.000	0.000	4.3 [b]
	800	700	0.000	0.000	4.3 [b]
35.0	170	100	0.103	0.745	2.43
	348	100	0.103	0.745	5.92
	348	100	0.103	0.745	6.60
	563	100	0.103	0.745	11.7
40.0	90.2	100	0.103	0.736	4.68
	287	100	0.103	0.736	9.44
	313	100	0.103	0.736	13.9
	376	100	0.103	0.736	12.8
	540	100	0.103	0.736	21.0
	550	100	0.103	0.736	22.0
	160	100	0.498	3.56	1.31
	306	100	0.498	3.56	2.27
	334	100	0.498	3.56	3.00
	490	100	0.498	3.56	4.08
	112	100	1.00	7.14	0.396
	503	100	1.00	7.14	2.10
	921	100	1.00	7.14	3.52
44.5	138	100	0.103	0.720	12.8
	371	100	0.103	0.720	35.0
	426	100	0.103	0.720	38.5
	483	100	0.103	0.720	52.0
	522	100	0.103	0.720	53.7

[a] Mol ratio of CO in cylinder; $P_{tot} = 1.02$ atm, including solvent vapour pressure. [b] Initial approximate values (see text).

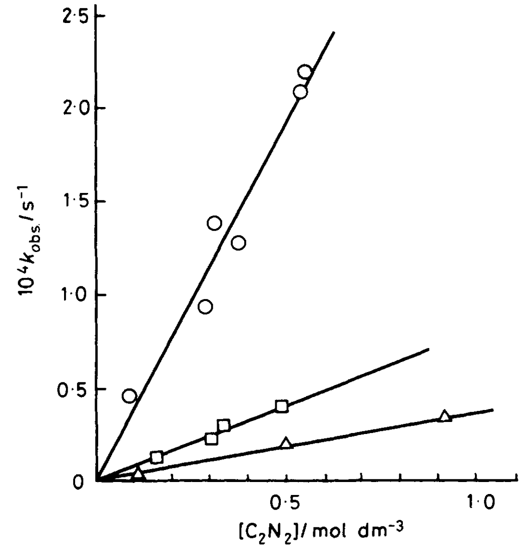


Figure 1. Plots of $k_{obs.}$ vs. $[C_2N_2]$ at 40 °C and various CO concentrations: 0.736×10^{-3} (○), 3.56×10^{-3} (□), and 7.15×10^{-3} mol dm^{-3} (△)

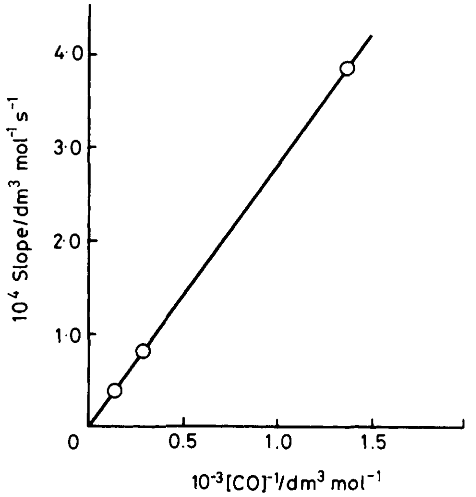


Figure 2. The slopes of Figure 1 plotted against the reciprocal of the CO concentration

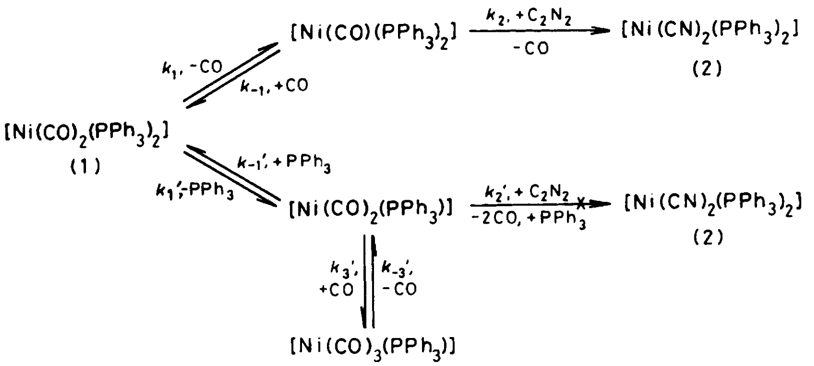
accumulation of $[Ni(CO)_3(PPh_3)]$, which becomes negligible for $[PPh_3]/[CO] \geqslant 15$. As a consequence all kinetic runs were performed in the presence of PPh_3 at constant p(CO). Using an appropriate excess of C_2N_2, $[C_2N_2]/[(1)] \geqslant 20$, the usual plots of log A_t vs. t were linear over three half-lives, indicating that the reaction rate is first order in complex concentration.

The observed reaction rate increases with increasing C_2N_2 concentration. Plots of $k_{obs.}$ vs. $[C_2N_2]$ are linear in the explored concentration range, with zero intercept (Figure 1). Carbon monoxide has a strong inhibiting effect and the $k_{obs.}$ values are linearly dependent on $[CO]^{-1}$ (Figure 2). Again there is no effect of PPh_3 concentration on the reaction rate. On the basis of these data, the experimental rate law takes the form $-d[(1)]/dt = k[(1)][C_2N_2]/[CO]$.

All $k_{obs.}$ values at 30.0, 35.0, 40.0, and 44.5 °C are collected in Table 1.

The behaviour so far described is consistent with a reaction mechanism involving preliminary ligand dissociation, as already found in ligand-exchange reactions of tetrakis nickel(0) complexes.[7,8] An overall view of the reaction pathway involved is given in the Scheme. Complex (1) may release either a PPh_3 or a CO group to give the corresponding reactive three-co-ordinate nickel(0) intermediates. The pathway involving PPh_3 dissociation is responsible for the observed accumulation of $[Ni(CO)_3(PPh_3)]$ in the absence of added PPh_3, but it is shown to be unproductive as regards $[Ni(CN)_2(PPh_3)_2]$ formation as follows: (*a*) free PPh_3 does not have any inhibiting effect on the rate of reaction (i); (*b*) $[Ni(CO)_3(PPh_3)]$, formed *in situ* by reaction of complex (1) with CO (7.2 mol dm^{-3}), does not react (30.0 °C, 48 h) with C_2N_2 (1.0 mol dm^{-3}) in the presence of the released PPh_3 (*ca.* 7.5×10^{-3} mol dm^{-3}). Bearing in mind that at this temperature the equilibration rate of $[Ni(CO)_3(PPh_3)]$ to $[Ni(CO)_2(PPh_3)_2]$ is fairly high,[7] and that this equilibrium involves the reactive $[Ni(CO)_2(PPh_3)]$ intermediate, this indicates that this intermediate has little reactivity towards C_2N_2 compared with CO or PPh_3. On the contrary, the data are fully consistent with a preliminary CO dissociation (k_1) followed by competitive C_2N_2 attack on the three-co-ordinate $[Ni(CO)(PPh_3)_2]$ complex (k_2) to give the product $[Ni(CN)_2(PPh_3)_2]$.

A rate law for the mechanism in the Scheme can easily be obtained under the present experimental conditions in which no accumulation of three-co-ordinate intermediates or by-products like $[Ni(CO)_3(PPh_3)]$ or $[Ni(CO)(PPh_3)_3]$ is observed. By applying the steady-state treatment to the $[Ni(CO)(PPh_3)_2]$ intermediate, the integrated rate equation (ii) is obtained.



Scheme.

$$k_{obs.} = \frac{k_1k_2[C_2N_2]}{k_{-1}[CO] + k_2[C_2N_2]} \qquad \text{(ii)}$$

If it is assumed that k_{-1}[CO] is $\gg k_2[C_2N_2]$, this equation reduces to the form experimentally determined, where $k = k_1k_2/k_{-1}$.

The reported kinetic parameters (Table 2) were obtained by a least-squares analysis of the data. The same percentage standard deviation in $k_{obs.}$ was assumed for each value of an homogeneous set of data at a given temperature. All the tabulated uncertainties are standard deviations corrected for the number of degrees of freedom, so that estimates of 95% confidence limits can be made by doubling the uncertainties.

The k values range from 1.27 × 10^{-7} s^{-1} (at 35 °C) to 6.97 × 10^{-7} s^{-1} (at 44.5 °C). These data cannot easily be interpreted in that they concern the composite rate function k_1k_2/k_{-1}. However, some insight can be gained by considering that the good linearity of the $k_{obs.}$ *vs.* [C$_2$N$_2$] plot implies that in the explored concentration range k_{-1}[CO] is at least ten times greater than $k_2[C_2N_2]$, *i.e.* $k_{-1}/k_2 \geqslant 7 \times 10^3$. The following lower limits can, therefore, be calculated: $k_1 \geqslant 8.9 \times 10^{-4}$, $\geqslant 2.0 \times 10^{-3}$, and $\geqslant 4.9 \times 10^{-3}$ s^{-1} at 35.0, 44.0, and 44.5 °C, respectively. These values are not inconsistent with those obtained, at 25 °C, for carbon monoxide dissociation from [Ni(CO)$_4$] (1.2 × 10^{-2} s^{-1} in hexane)[8] and from [Ni(CO)$_3$(PPh$_3$)] (5.7 × 10^{-4} s^{-1} in cyclohexane).[7]

A more detailed comment upon the very high k_{-1}/k_2 ratio and the lack of any inhibiting effect played by PPh$_3$ on the reaction rate is required. This behaviour is clearly in contrast with previous observations, *i.e.* the lack of discriminating ability of three-co-ordinated nickel(0) intermediates towards entering ligands. For example, a k(CO)/k(PPh$_3$) ratio equal to 0.2 for nucleophilic attack on [Ni(CO)$_3$][8] and k(C$_2$N$_2$)/k(dppb) ratio equal to *ca.* 20 for attack on [Ni(CO)(dppb)] (dppb = Ph$_2$P[CH$_2$]$_4$PPh$_2$) have been reported.[9] The remarkable discrimination towards CO, C$_2$N$_2$, and PPh$_3$ exhibited by [Ni(CO)(PPh$_3$)$_2$] can be explained as follows. Bimolecular attack of PPh$_3$ or CO on the reactive three-co-ordinate intermediate gives *directly* the corresponding complexes, and, as a consequence, the observed large discrimination is easily attributed to predominant steric factors which favour nucleophilic attack of CO compared with that of the much larger PPh$_3$.

By contrast, the competition ratio k_{-1}/k_2 does not simply represent, in principle, the discriminating ability of [Ni(CO)(PPh$_3$)$_2$] towards bimolecular attack of CO and C$_2$N$_2$, in that the reaction step represented by k_2 involves a number of events: (*a*) cyanogen addition; (*b*) C–C bond breaking of the C$_2$N$_2$ ligand and parallel oxidation of Ni^0 to Ni^{II}; (*c*) successive (or concomitant) carbon monoxide release. If steps (*b*) and (*c*) are much faster than (*a*), k_{-1}/k_2 is really a measure of the discrimination towards nucleophilic attack; but, in this case, its very high value ($\geqslant 7 \times 10^3$) cannot easily be justified on the basis of steric and electronic differences between the entering CO and C$_2$N$_2$ ligands. It seems more reasonable to assume that the intermediate [Ni(CO)(C$_2$N$_2$)(PPh$_3$)$_2$] derived from step (*a*) can either quickly lose C$_2$N$_2$ to reform [Ni(CO)(PPh$_3$)$_2$] (k_{-a}) or undergo a slow C–C bond breaking of the C$_2$N$_2$ ligand to give the oxidation product [Ni(CN)$_2$(PPh$_3$)$_2$] (k_b). In this hypothesis k_2 is a complex function of the rate constants of these elementary steps, *i.e.* $k_2 = k_ak_b/k_{-a}$, and the real value of the rate constant for C$_2$N$_2$ attack (k_a) is substantially higher than k_2.

Table 2. Kinetic parameters [a] of reaction (i) obtained according to the rate equation $k_{obs.} = k[C_2N_2]/[CO]$

θ_c/°C	$10^7k(= k_1k_2/k_{-1})$/s^{-1}
35.0	1.27 (0.17) [b]
40.0	2.84 (0.05) [c]
44.5	6.97 (0.32) [b]

$\Delta H^‡$ = 156(8) kJ mol^{-1}, $\Delta S^‡$ = 128(25) J K^{-1} mol^{-1}.

[a] Standard deviations in parentheses (see text). [b] $\sigma(k_{obs.})$ = 26.4% at 35.0 °C and 10.3% at 44.5 °C. [c] Weighted average of three sets at [CO] = 0.736 × 10^{-3} [$\sigma(k_{obs.})$ = 21.3%], 3.56 × 10^{-3} [$\sigma(k_{obs.})$ = 13.0%], and 7.15 × 10^{-3} mol dm^{-3} [$\sigma(k_{obs.})$ = 18.1%].

In accord with this reasoning, [Ni(CO)$_2$(PPh$_3$)] exhibits a much lower reactivity towards C$_2$N$_2$ than PPh$_3$. This behaviour may be accounted for by the lower oxidizability (lower k_b term) expected for a complex bearing two CO and one PPh$_3$ instead of two PPh$_3$ and one CO ligands.

The activation parameters for k($\Delta H^‡$ = 156 kJ mol^{-1} and $\Delta S^‡$ = 128 J K^{-1} mol^{-1}) can be briefly discussed on the basis of the above. If one considers that $\Delta H^‡$ corresponds to $\Delta H_1^‡ + \Delta H_2^‡ - \Delta H_{-1}^‡$ and that $\Delta H_2^‡$ should be greater than $\Delta H_{-1}^‡$, the value of 156 kJ mol^{-1} is an upper limit for $\Delta H_1^‡$, the activation enthalpy for CO dissociation from [Ni(CO)$_2$(PPh$_3$)$_2$]. A value of 101 kJ mol^{-1} was found for CO dissociation from [Ni(CO)$_4$].[8] Also the large positive activation entropy is characteristic of a dissociative process and should mainly correspond to $\Delta S_1^‡$.

The results obtained in this study confirm that C$_2$N$_2$ readily reacts with metal complexes in low oxidation states to give oxidative addition. As in the case of [Ni(CO)(dppb)$_2$],[9] preliminary slow ligand dissociation is followed by co-ordination of C$_2$N$_2$ to the metal centre and by oxidative addition with C–C bond breaking of the cyanogen moiety.

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