Inorganica Chimica Acta, *133* (1987) 267–274

Kinetics of 1,3-Dipolar Cycloadditions of Dimethylacetylenedicarboxylate to $LCo(AcAc)_2N_3$

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(Received February 4, 1987)

Abstract

A series of $LCo(AcAc)_2N_3$ complexes (where AcAc is the monoanion of 2,4-pentanedione and L is $(p\text{-}ClC_6H_4)_3P$, $(C_6H_5)_3P$, $(p\text{-}CH_3C_6H_4)_3P$, $(p\text{-}CH_3OC_6H_4)_3P$, 1-phenyldibenzophosphole or pyridine) have been prepared and characterized by infrared, ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, cyclic voltammetry and elemental analyses. All the phosphine complexes are *cis* and the pyridine complexes have been isolated as both *cis* and *trans* isomers. In solution the pyridine complexes exist as an equilibrium mixture of the two isomers with the *cis* isomer predominating ($k_{eq} = 2.49$). The isomerization process is relatively slow; $t_{1/2} = 40$ min for approach to equilibrium. These complexes undergo 1,3-dipolar cycloaddition reactions with dimethylacetylenedicarboxylate (DAD) to produce *trans* isomers of $LCo(AcAc)_2X$ where X is the N(2)-bound 4,5-bis(methoxycarbonyl)-1,2,3-triazolate. The kinetics of these reactions have been investigated by infrared spectroscopy. For the $PyCo(AcAc)_2N_3$ complexes the cycloaddition reactions are associative, second-order processes with rates that are independent of the geometry of the complex. The cycloaddition reactions of the $R_3PCo(AcAc)_2N_3$ complexes are first-order processes with rates that are independent of the DAD concentration. For the $(p\text{-}x\text{-}C_6H_5)_3PCo(AcAc)_2N_3$ complexes, the rates of the cycloaddition reactions are linearly related to the Hammet σ constants of the *para* substituents and increase with decreasing basicity of the triarylphosphine. The rates of these reactions are also related to the reduction potentials (determined by cyclic voltammetry) of the azide complexes and increase with increasing ease of reduction. A mechanism is proposed for these reactions.

Introduction

We have recently reported the synthesis [1] of a variety of cobalt(III) triazolate complexes by 1,3-dipolar cycloadditions of $CH_3CO_2C{\equiv}CCO_2CH_3$ (DAD) to cobalt azide complexes and the kinetics of the reactions [2] of a series of *trans*-$LCo(DH)_2N_3$ complexes (where DH is the monoanion of dimethylglyoxime) with DAD. We observed that the rates of the $LCo(DH)_2N_3$ + DAD reactions were influenced only slightly by the nature of the ligand *trans* to azide. The fastest reaction was only 3.5 times faster than the slowest for ligands, L, with a wide range of donor abilities, indicating that in this system the *trans* effect is not very large. However, changing the nature of the chelating ligand *cis* to the azide brought about a change in the rate constant for the cycloaddition reactions of about two orders of magnitude [1]. It is usually found that the *cis* effect is smaller than the *trans* effect [3] for most metal complexes unless steric factors become important [3, 4]. In order to gain information regarding the nature of the *cis* effect and the steric effect on the 1,3-dipolar cycloaddition to coordinated azide we prepared a series of complexes of the type *cis*-$LCo(AcAcc)_2N_3$, where AcAc is the monoanion of 2,4-pentanedione and L = $(p\text{-}ClC_6H_4)_3P$, $(C_6H_5)_3P$, $(p\text{-}CH_3C_6H_4)_3P$, $(p\text{-}CH_3OC_6H_4)_3P$, 1-phenyldibenzophosphole (DBP), and pyridine, and determined the rates of their 1,3-dipolar cycloaddition reactions (eqn. (1)) with DAD. The results of these studies are described herein.

Experimental

Materials

Commercially available reagents were reagent grade and were used as received if they contained no IR or NMR detectable contaminants. Otherwise

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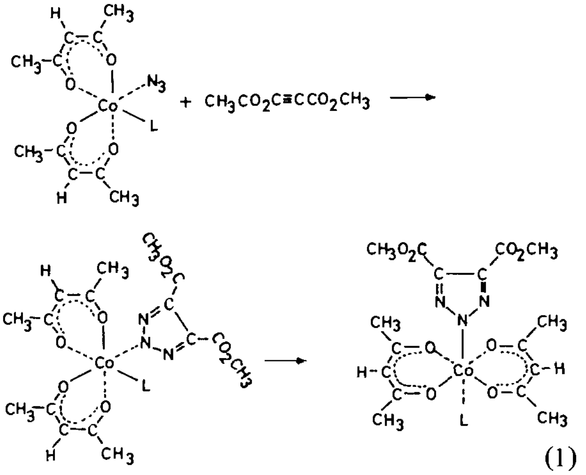


(1)

they were purified by standard procedures. The *para* substituted triarylphosphines were prepared by standard Grignard syntheses from PCl_3 [5]. 1-Phenyldibenzophosphole (DBP) was prepared by a modification of the procedure of Cornforth *et al.* [6]. The chloroform used for kinetic measurements was acid washed to remove the ethanol stabilizer, doubly distilled over calcium chloride, checked by ^1H NMR spectroscopy for purity, kept in the dark, and used the same day it was distilled. Dimethylacetylenedicarboxylate (Aldrich) was distilled under reduced pressure (boiling point 90 °C, 15 mm) just prior to kinetic studies. The $LCo(AcAc)_2N_3$ complexes were prepared by the following methods:

(a) L = PPh_3, $(p\text{-}CH_3OC_6H_4)_3P$ and DBP. To 3.5 g (13.6 mmol) $Co(AcAc)_2$ suspended in 400 ml absolute ethanol were added 0.9 g (13.6 mmol) NaN_3, 4 ml glacial acetic acid and 4 ml 10% H_2O_2, respectively. After the resulting solution was stirred vigorously for an hour at ambient temperature, a solution of the ligand (L, 13.6 mmol) in 10 ml hot absolute ethanol was added. The solution volume was then reduced to about 100 ml with the aid of an aspirator overnight and a dark green product precipitated. The product was isolated by filtration, washed with anhydrous diethylether, vacuum dried and recrystallized from $CHCl_3/CH_3CH_2OH$ containing a small amount of the respective phosphine. A typical yield was 65%. $Ph_3PCo(AcAc)_2N_3$, melting point (m.p.) 132–133 °C; literature value 132–133 °C [7]; $DBPCo(AcAc)_2N_3$ m.p. 131–132 °C, $(p\text{-}CH_3OC_6H_4)_3PCo(AcAc)_2N_3$, m.p. 110–111 °C.

(b) L = $(p\text{-}ClC_6H_4)_3P$ and $(p\text{-}CH_3C_6H_4)_3P$. Solutions containing 1.794 g (3.000 mmol) $Co_2(AcAc)_4(N_3)_2$ [8] and 6.0 mmoles of the phosphine in 30 ml of $CDCl_3/CHCl_3$ were stirred magnetically at ambient temperature and the progress of the reaction monitored by ^1H NMR spectroscopy. After one week the reaction was complete and the solution was reduced to dryness on a rotary evaporator. The dark green products were recrystallized from C_2H_5OH/H_2O mixtures containing a small amount of the respective phosphine to give 3.2 g (89%) $(p\text{-}ClC_6H_4)_3PCo(AcAc)_2N_3$, decomposition point (d.p.) 101 °C and 3.5 g (88%) $(p\text{-}CH_3C_6H_4)_3PCo(AcAc)_2N_3$, d.p. 91 °C.

(c) *trans*- and *cis*-$PyCo(AcAc)_2N_3$ and $Co_2(AcAc)_4(N_3)_2$ were prepared by the literature methods [7, 8].

All the complexes were recrystallized three times, vacuum dried at ambient temperature overnight and checked for purity by infrared spectroscopy, ^1H, $^{13}C\{^1H\}$ and where appropriate $^{31}P\{^1H\}$ NMR spectroscopy. Satisfactory carbon and hydrogen analyses were obtained from Galbraith Laboratories, Knoxville, Tenn. 37921, for all complexes.

Spectroscopic Measurements

Infrared spectra were recorded on a Perkin-Elmer 599 spectrometer as KBr pellets and as chloroform solutions in 0.1 mm sealed NaCl cells. The ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded at 99.54, 25.00 and 40.26 MHz, respectively, on a JEOL FX-100Q spectrometer in the FT mode. Proton and carbon chemical shifts are downfield relative to internal Me_4Si, while the phosphorus chemical shifts were measured relative to external PPh_3 ($\delta = -6.0$ ppm) and corrected to 85% H_3PO_4. A positive sign on the phosphorus chemical shift indicates a downfield position relative to H_3PO_4.

Cyclic Voltammetry

All cyclic voltammograms were recorded at 25 ± 0.1 °C in dichloromethane containing 0.1 M tetrabutylammonium perchlorate (TBAP) and in acetonitrile containing 0.1 M tetraethylammonium perchlorate (TEAP) using an EG & G PAR electrochemical system consisting of a model RE0073 recorder, a model 173 potentiostat and a model 175 universal programmer. A three electrode system with instrumental IR compensation was used throughout. The working and auxiliary electrodes were a platinum disk and wire respectively. The reference electrodes for dichloromethane/TBAP and acetonitrile/TEAP systems were $Ag/AgCl(CH_2Cl_2$; saturated LiCl) and aqueous calomel, respectively. The test solution was separated from the reference electrode by a salt bridge containing a Vycor plug and was filled with the corresponding solvent/supporting electrolyte system. Temperature regulation was achieved with a Brinkman Lauda K-2/R temperature controller with the electrochemical cell immersed in the constant temperature bath. As recommended by IUPAC [9] for electrochemistry in non-aqueous solvents, the ferricinium ion (Fc^+)/ferrocene (Fc) couple was employed as the reference, and all potentials reported herein are given *versus* this couple. As suggested by Gagné *et al.* [10] whenever possible, ferrocene was used as an internal standard to compensate for the junction potential variability among experiments. TEAP (Fluka, purum) and TBAP (Fluka, purum) were recrystallized from ethanol/water and dried under vacuum at 100 °C overnight. Dichloromethane ('Baker Analyzed', Reagent) and acetonitrile (Aldrich, gold label, spectroscopic grade) were dried over Linde 4 Å molecular sieves.

Kinetic Studies

Solutions containing 3.75×10^{-4} mol of the azide complex and 3.75×10^{-3} mol of dimethylacetylenedicarboxylate in 30 ml freshly distilled chloroform were contained in a 50 ml two-necked round bottom flask. The center neck of the flask was surmounted with a water-cooled condensor and a calcium chloride drying tube and the side neck was closed with a rubber syringe septum. The flask was immersed in a Brinkman Lauda K-2/R temperature bath maintained ($T \pm 0.1$ °C) at the desired temperature. Aliquots were withdrawn periodically from this flask by syringe and the $\nu(N_3)$(asym) absorbance at about 2025 cm^{-1} measured as a function of time in 0.1 mm sealed NaCl cells. Three repetitive scans were made between 2100 and 2001 cm^{-1} with a 5X wavelength expansion and an ordinate expansion of 3. The lower energy limit was set at 2001 cm^{-1} in order to avoid a lengthy grating change at 2000 cm^{-1}. All kinetic data are the average of at least three such experiments. Beer's law behavior was verified for the $\nu(N_3)$(asym) vibration for each complex over the concentration range studied. The reactions were followed for at least three half lives and in most cases until the reaction was 95% complete. The kinetic data were plotted and analyzed by a linear least-squares curve fitting computer program [11] and six to twelve points were included in all plots except for the $(p\text{-}ClC_6H_4)_3PCo(AcAc)_2N_3$ reaction where only three data points could be obtained because of the rapid rate of this reaction.

Results and Discussion

Characterization of the Complexes

The complexes, $LCo(AcAc)_2N_3$, may exist in *cis* and *trans* isomeric forms. The ^1H and $^{13}C\{^1H\}$ NMR data (Table I) indicated that, except for the pyridine complex, all these complexes exist as the *cis* isomer in solution as four resonances are observed for the AcAc methyl groups and carbonyl carbons and two resonances are observed for the methine protons and carbons. The pyridine complex may be isolated in both isomeric forms [8]. Upon dissolution of either the *cis*- or *trans*-$PyCo(AcAc)_2N_3$ complex in chloroform an equilibrium (eqn. (2)) is slowly established.

$$trans\text{-}PyCo(AcAc)_2N_3 \overset{K}{\rightleftharpoons} cis\text{-}PyCo(AcAc)_2N_3 \qquad (2)$$

At 29 °C the equilibrium constant is 2.49 and $t_{1/2}$ for approach to equilibrium is 40 min (both were determined by integration of the ^1H methine resonances as a function of time). This isomerization has been previously noted [8]. Repeated attempts to isolate the *trans* isomers for the phosphorus donor ligands were unsuccessful. However, in the ^1H NMR spectra of each of these complexes there is always an additional very small methine resonance and a very small methyl resonance (Fig. 1 shows a typical spectrum) suggesting the presence of minor amounts of the *trans* isomers in solution. Attempts to verify this suggestion by $^{31}P\{^1H\}$ NMR spectroscopy were unsuccessful as for example the $^{31}P\{^1H\}$ NMR of PPh_3Co-

TABLE I. ^1H and ^{13}C NMR Data for the Complexes $LCo(AcAc)_2N_3$, δ (ppm) in $CDCl_3$

	$\delta\,^1H$ (ppm)		$\delta\,^{13}C$ (ppm)		
L	CH_3	CH	CH_3	CH	CO
$(p\text{-}ClC_6H_4)_3P$	1.70, 1.72, 1.93, 2.31	5.07, 5.50	26.1, 26.3, 26.9, 27.1	96.6	186.1, 188.6, 189.9, 190.0
$(C_6H_5)_3P$	1.67, 1.72, 1.91, 2.29	5.02, 5.48	26.2, 26.9, 27.2	96.5, 97.4	186.3, 188.3, 188.7, 189.7
$(p\text{-}CH_3C_6H_4)_3P$	1.64, 1.94, 2.33[a], 2.40	5.03, 5.48	21.2[a], 26.0, 26.2, 26.9, 27.2	96.5, 97.5	186.2, 188.1, 189.3, 189.6
$(p\text{-}CH_3OC_6H_4)_3P$	1.68, 1.86, 1.92, 2.29, 3.81[a]	5.03, 5.47	26.2, 26.4, 27.0, 27.4, 55.1[a]	96.7, 97.5	186.3, 188.2, 189.5, 189.7
1-phenyldibenzophosphole	1.44, 1.50, 1.98, 2.32	4.76, 5.52	26.2, 26.6, 27.3, 27.6	97.1	186.5, 188.7, 190.3, 190.4
pyridine	2.05, 2.17, 2.23, 2.24	5.40, 5.57	26.1, 26.4, 26.5, 26.9	97.1, 97.4	188.6, 189.1, 190.0
pyridine[b]	2.17	5.36	26.5	97.8	190.0

[a] $ArCH_3$. [b] *trans* isomer.

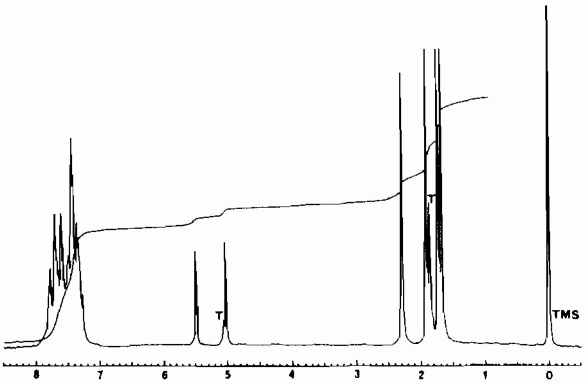
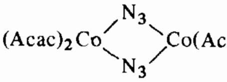


Fig. 1. 100 MHz ^1H NMR spectrum of $PPh_3Co(AcAc)_2N_3$ in $CDCl_3$ at 30 °C. Resonances marked T are attributed to *trans*-$PPh_3Co(AcAc)_2N_3$.

$(AcAc)_2N_3$ in $CDCl_3$ at 32 °C showed a very broad resonance ($\nu_{1/2} = 2000$ Hz) at δ 6.2 ppm. This resonance remains broad in the presence of excess PPh_3. The breadth of this resonance is probably due to a combination of cobalt quadrupole broadening [12] and ligand exchange. The phosphorus coordination chemical shift, $\Delta\delta$ ^{31}P, (defined as $\Delta\delta^{31}P = \delta^{31}P$ (complex) $- \delta$ ^{31}P (ligand)) of 12.2 ppm for PPh_3-$Co(AcAc)_2N_3$ is considerably less than that found for $PPh_3Co(DH)_2N_3$ (28.9 ppm) [2] suggesting that the cobalt phosphorus bond is weaker in the AcAc complex than in the oxime complex. $Ph_3PCo(AcAc)_2N_3$ may only be crystallized from a solution containing excess PPh_3.

The values of the infrared stretching frequencies, $\nu(N_3)$(asym) (Table II) are nearly the same in the solid state and in solution suggesting that the solid state and solution geometries are the same. But note that there is essentially no difference in $\nu(N_3)$ for *cis*- and *trans*-$pyCo(AcAc)_2N_3$, so that $\nu(N_3)$ is not a good criterion for the determination of the complex geometry. The $LCo(AcAc)_2N_3$ complexes all exhibit this vibration around 2025 cm^{-1} which is slightly higher in energy than what was found for the analogous $LCo(DH)_2N_3$ complexes [2] (*ca.* 2018 cm^{-1}).

TABLE II. Azide Stretching Frequencies, $\nu(N_3)$(asym), for the Complexes $LCo(AcAc)_2N_3$

L	$\nu(N_3)$ in $CHCl_3$ (cm^{-1})	$\nu(N_3)$ in KBr (cm^{-1})
$(p\text{-}ClC_6H_4)_3P$	2023	2021
Ph_3P	2029	2016
DBP	2029	2021
$(p\text{-}CH_3C_6H_4)_3P$	2030	2021
$(p\text{-}CH_3OC_6H_4)_3P$	2017	2009
Py[a]	2025	2021
Py	2024	2020
 $(Acac)_2Co\overset{N_3}{\underset{N_3}{<>}}Co(AcAc)_2$	2029, 2072	2072

[a] *trans isomer.*

Cycloaddition Reactions

These complexes react cleanly and in high yield with DAD according to eqn. (1) to produce triazolate complexes which all have the *trans* geometry and contain N(2) bound triazolate [1]. The rates of eqn. (1) have been investigated under pseudo-first-order conditions by infrared spectroscopic monitoring of the decrease in intensity of the $\nu(N_3)$(asym) vibration for the $LCo(AcAc)_2N_3$ complexes in the presence of a ten to one molar ratio of DAD to complex. For *cis*- and *trans*-$PyCo(AcAc)_2N_3$ the reactions are overall second-order, first-order in each reactant, as shown by the data in Table III. These data conform to the rate law; rate = k_{obs} [$PyCo(AcAc)_2N_3$], where $k_{obs} = k'$[DAD]. As the data in Table IV show, the rate of these reactions is the same for the *cis* and *trans* $PyCo(AcAc)_2M_3$ complexes. This is because the isomerization rate for these complexes (eqn. (2)) is faster than the rate of cycloaddition. The rates of these cycloaddition reactions are an order of magnitude greater than the analogous reaction with $PyCo(DH)_2N_3$ [2]. Under identical conditions $k_{obs} = 5 \times 10^{-5}$ s^{-1} for $PyCo(AcAc)_2$-N_3 and 7×10^{-6} s^{-1} for $PyCo(DH)_2N_3$.

In contrast to the reactions of $PyCo(AcAc)_2N_3$, the reactions of the $R_3PCO(AcAc)_2N_3$ complexes with DAD were found to be first order and independent of the DAD concentration (Table III). Figure 2 shows a typical pseudo-first-order kinetics plot of ln[$LCo(AcAc)_2N_3$] *versus* time. Several experiments have been conducted in an attempt to explain this behavior. The infrared spectrum of a solution containing 3.75×10^{-4} mol of *cis*-$PPh_3Co(AcAc)_2N_3$

TABLE III. Influence of DAD and $LCo(AcAc)_2N_3$ Concentrations on the Rate of eqn. (1) in $CHCl_3$ at 27 °C

L	10^3 [$LCo(AcAc)_2N_3$]	10 [DAD]	k_{obs} (s^{-1})[a]
PPh_3	6.27	1.25	2.00×10^{-3}
PPh_3	12.5	0.63	1.50×10^{-3}
PPh_3	12.5	1.25	1.36×10^{-3}
PPh_3	12.5	2.50	1.43×10^{-3}
PPh_3	12.5	3.75	1.49×10^{-3}
PPh_3	12.5	5.00	1.60×10^{-3}
DBP	6.25	1.25	6.42×10^{-4}
DBP	12.5	1.25	5.05×10^{-4}
DBP	12.5	2.50	6.20×10^{-4}
t-Py	6.25	1.25	6.03×10^{-5}
t-Py	12.5	1.25	5.09×10^{-5}
t-Py	12.5	2.50	9.78×10^{-5}

[a] k ± 0.05.

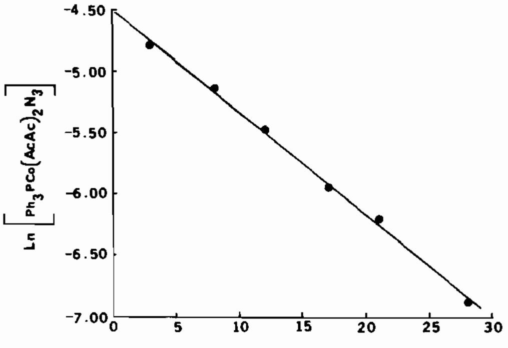
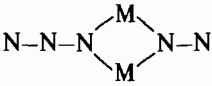


Fig. 2. Pseudo-first-order rate plot for the reaction of PPh_3-$Co(AcAc)_2N_3$ (0.0125 M) with $CH_3CO_2C{\equiv}CCO_2CH_3$ (0.125 M) in $CHCl_3$ at 27 °C. Similar data were obtained for all the $R_3PCo(AcAc)_2N_3$ complexes listed in Table IV.

in 30 ml $CHCl_3$, displayed a major azide vibration at 2030 cm^{-1} and a very weak vibration at 2070 cm^{-1}. Immediately after injecting 3.75×10^{-3} mol of DAD into this solution the 2070 cm^{-1} absorption increased in intensity slightly. As time progressed, the intensity of the 2030 cm^{-1} absorption decreased exponentially two orders of magnitude faster than did the 2070 cm^{-1} absorption. Over a period of 24 h the intensity of both absorptions decreased to zero and $PPh_3Co(AcAc)_2$triazolate [2] was isolated from the solution in greater than 90% yield. It appears that the 2070 cm^{-1} absorption is due to some species that is formed from $PPh_3Co(AcAc)_2N_3$ that reacts with DAD at a much slower rate.

The azide bridged dimer $Co_2(AcAc)_4(N_3)_2$ which is believed to contain asymmetric azide bridges,  $\mathrm{N{-}N{-}N}\begin{smallmatrix}\mathrm{M}\\ \\ \mathrm{M}\end{smallmatrix}\mathrm{N{-}N{-}N}$ [13], was prepared and found to exhibit $\nu(N_3)$ at 2072 (strong) and 2029 (weak) cm^{-1} in $CHCl_3$. Its ^1H NMR spectrum (Fig. 3) showed

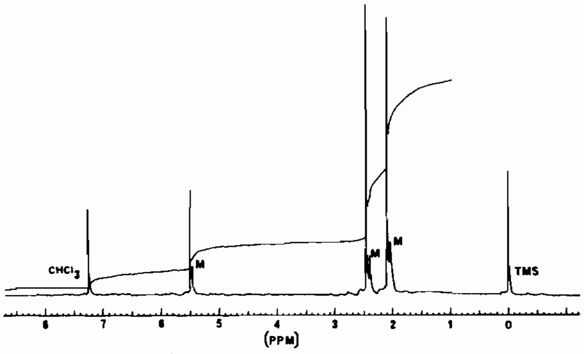


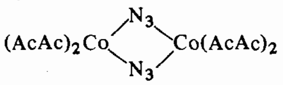
Fig. 3. 100 MHz ^1H NMR spectrum of $Co_2(AcAc)_4(N_3)_2$ in $CDCl_3$ at 30 °C. Resonances marked M are attributed to $Co(AcAc)_2N_3$.

the presence of two species. The major resonances assigned to the dimer occur at δ 2.09, 2.46 (CH_3); and 5.50 ppm (CH) and minor resonances assigned to the monomer $Co(AcAc)_2N_3$ occur at δ 2.05, 2.4 (CH_3); and 5.48 ppm (CH). Its $^{13}C\{^1H\}$ spectrum in $CDCl_3$ showed only resonances due to the dimer at δ25.5, 26.7 (CH_3); 96.4 (CH), 188.9 and 190.2 ppm (CO). The observation of separate ^1H resonances for the monomer and dimer indicate that the exchange rate between the dimer and the monomer is no greater than 8.66 s^{-1} based upon the average chemical shift difference of 3.90 Hz for the various proton resonances for these two species and the equation $k = (2/\pi\delta\nu)^{-1}$. Based upon the intensity ratios of the resonances of the dimer and monomer (3:1 on a mole basis) the equilibrium favors the dimer and

$$k_{eq} = \frac{k_f}{k_r} = \frac{[Co_2(AcAc)_4(N_3)_2]_2}{[Co(AcAc)_2N_3]} = 3$$

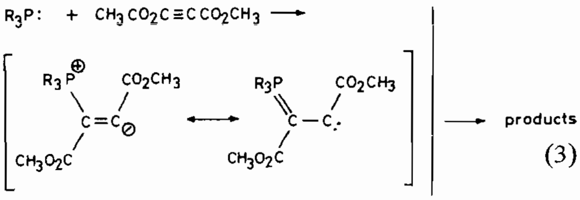
The average exchange rate constant is $(k_f + k_r)/2 = 8.66\ s^{-1}$. Thus $k_r \geqslant 4.33\ s^{-1}$ and $k_f \geqslant 12.99\ s^{-1}$. The rate of formation of the monomer $Co(AcAc)_2N_3$ from the dimer $Co_2(AcAc)_4(N_3)_2$ is relatively fast

TABLE IV. Rate Data[a] for the Reactions $LCo(AcAc)_2N_3 + CH_3CO_2C{\equiv}CCO_2CH_3 \rightarrow LCo(AcAc)_2$triazolate in Chloroform at 27 °C

L	k_{obs} (s^{-1})[c]	$t_{1/2}$ (min)	$\Sigma\sigma p$[b]	log k_X/k_H
$(p\text{-}ClC_6H_4)_3P$	7.96×10^{-3}	1	0.69	0.77
Ph_3P	1.36×10^{-3}	8	0.00	0
DBP	5.05×10^{-4}	23		
$(p\text{-}CH_3C_6H_4)_3P$	2.85×10^{-4}	41	−0.51	−0.68
$(p\text{-}CH_3OC_6H_4)_3P$	1.07×10^{-4}	108	−0.81	−1.10
Py[d]	5.09×10^{-5}	227		
Py[e]	4.82×10^{-5}	240		
 $(\mathrm{AcAc})_2\mathrm{Co}\begin{smallmatrix}\mathrm{N_3}\\ \\ \mathrm{N_3}\end{smallmatrix}\mathrm{Co(AcAc)_2}$	1.38×10^{-5}	837		

[a] $[LCo(AcAc)_2N_3] = 0.0125$ M; $[CH_3CO_2C{\equiv}CCO_2CH_3] = 0.125$ M. [b] Ref. 20. [c] $k \pm 0.05$. [d] *trans* isomer. [e] *cis* isomer.

compared with the rate of attack of either ($(p\text{-}ClC_6H_4)_3P$ or $(p\text{-}CH_3C_6H_4)_3P$ on $Co_2(AcAc)_4(N_3)_2$ to form respectively $(p\text{-}ClC_6H_4)_3PCo(AcAc)_2N_3$ and $(p\text{-}CH_3C_6H_4)_3PCo(AcAc)_2N_3$ which had a half life by ^1H NMR (see 'Experimental) of about 3 days. Upon dissolution of $R_3PCo(AcAc)_2N_3$ in $CDCl_3$ the infrared spectra show that only a small amount of $Co_2(AcAc)_4(N_3)_2$ is present in the solution. Thus, dissociation of R_3P from $R_3PCo(AcAc)_2N_3$ occurs only to a small extent but it is rapid and cleavage of the dimer by phosphine is slow. Addition of excess phosphine to a solution of $R_3PCo(AcAc)_2N_3$ should decrease the amount of dimer formed and it should also affect the rate of the 1,3-dipolar cycloaddition reaction by reacting with DAD according to eqn. (3) [14–16].



(3)

Kinetic studies in the presence of excess PPh_3 (Table V) revealed that the rate of the cycloaddition is barely affected by the presence of excess PPh_3. We showed in a previous study of the cycloaddition reactions of $R_3PCo(DH)_2N_3$ with DAD [2] that the reactions involved cobalt(II) species. A kinetic study of the $PPh_3Co(AcAc)_2N_3$ reaction with DAD in the presence of the mild oxidizing agent $CBrCl_3$ [17] (Table V) showed that the reaction was not affected to a significant extent by $CBrCl_3$ in contrast to what was found for the $R_3PCo(DH)_2N_3$ reactions [2]. This suggests that $[Co^{II}(AcAc)_2N_3]^-$ reacts faster with DAD than with $CBrCl_3$.

For the triarylphosphine complexes, the rates are related to Hammett substituent parameters as illustrated in Table IV. The relationship is $\log k_X/k_H = \rho\Sigma\sigma_p$ where $\rho = +1.24$ ($r^2 = 0.997$). The rate increases with decreasing basicity of the phosphine.

TABLE V. Rate Data for the Reactions $(C_6H_5)_3PCo(AcAc)_2N_3 + CH_3CO_2C{\equiv}CCO_2CH_3 \rightarrow (C_6H_5)_3PCo(AcAc)_2$-triazolate in Chloroform at 27 °C[a]

Solvent	Excess ligand	$10^3\ k\ (s^{-1})$
$CHCl_3$	none	1.36
$CHCl_3$	0.0125 M PPh_3	1.39
95% $CHCl_3$ + 5% $CBrCl_3$	none	1.66

[a] $[Ph_3PCo(AcAc)_2N_3] = 0.0125$ M; $[CH_3CO_2C{\equiv}CCO_2CH_3] = 0.125$ M; $k \pm 0.05$.

Cyclic voltammetry experiments were performed on all the $LCo(AcAc)_2N_3$ complexes. The cyclic voltammograms in acetonitrile were time dependent indicating pronounced but slow dissociation of the ligand L, and the possible existence of other equilibria. Only potentials corresponding to the redox processes Co(III) ⇌ Co(IV) and Co(III) ⇌ Co(II) obtained in dichloromethane (where dissociation is less pronounced) are summarized in Table VI.

TABLE VI. Oxidation and Reduction Potentials of the $LCo(AcAc)_2N_3$ Complexes[a]

L	E_{pa} Co(III) ⇌ Co(IV)	E_{pc} Co(III) ⇌ Co(II)
$(p\text{-}ClC_6H_4)_3P$	0.93	−1.47
$(C_6H_5)_3P$	0.86	−1.65
DBP	0.88	−1.74
$(p\text{-}CH_3C_6H_4)_3P$	0.77	−1.80
$(p\ CH_3OC_6H_4)_3P$	0.82	−1.91
Py[b]	1.00	−1 48
Py[c]	1 01	−1.82
$Co_2(AcAc)_4(N_3)_2$	1.18, 1.36	−1.93[d]

[a] In CH_2Cl_2 containing 0.1 M TEAP at 25 °C, $V = 200$ mV s^{-1}; E (V) *vs.* Fc^+/Fc. [b] *trans* isomer. [c] *cis* isomer. [d] Very broad, peak current is nearly twice as large as that for each oxidation wave.

It may be seen from the data in Table VI that the ligand L in $LCo(AcAc_2N_3$ has only a small influence on the oxidation potentials. However, it has a relatively much larger influence on the reduction potentials. Also, the reduction potentials decrease with decreasing basicity of the phosphine in the complexes $R_3PCo(AcAc)_2N_3$. The weaker the cobalt ligand bond, the higher should be the positive charge density on the cobalt center and the lower should be the reduction potential for the process Co(III) ⇌ Co(II). There is a good linear correlation between the Hammett constants of the *para* substituents and the reduction potentials (E_{pc}) of the phosphorus ligand complexes of the form $\Sigma\sigma_p = 3.43\ E_{pc} + 5.70$ ($r^2 = 0.996$) similar to the relationship that Edwards [18] found between the nucleophilic constants of Swain and Scott [19] and the electrode potentials for a series of anions. Edwards [18] also found that for the same series of anions as well as for some neutral ligands there was a linear relationship between the logarithm of their complex formation constants with several metals and the electrode potentials of the ligands. Thus, one might expect to find a linear correlation between the logarithm of the rate constants for the cycloaddition reactions and the reduction potentials (E_{pc}) of the phosphorus ligand complexes. Indeed there is an excellent linear correlation of the form $\log k_X/k_H = 4.30\ E_{pc} + 7.08$ ($r^2 = 0.999$). We previously found a linear relation between the cycloaddition rate constants and the reduction potentials for the analogous $R_3PCo(DH)_2N_3$ complexes [2].

The cyclic voltammogram of $Co_2(AcAc)_4(N_3)_2$ in CH_2Cl_2 shows the existence of two species in solution as there are two oxidation waves and one broad reduction wave with a peak current nearly equal to twice that of either oxidation wave. The two oxidation waves could be due to $Co_2(AcAc)_4(N_3)_2$ and $Co(AcAc)_2N_3$ (*vide supra*).

The rates of the cycloaddition reactions of DAD with the *cis*-$LCo(AcAc)_2N_3$ complexes are all much faster than those found for the analogous *trans*-$LCo(DH)_2N_3$ complexes [2]. Also, for the *trans*-$LCo(DH)_2N_3$ complexes the cycloaddition rates were essentially independent of the nature of the ligands L *trans* to the azide. Consequently, the *cis* effect is much greater than the *trans* effect on these 1,3-dipolar cycloadditions. In line with this we found that the reactions of the complexes $PPh_3Co(BAE)N_3$, $Ph_3PCo(Salen)N_3$ and $Ph_3PCo(Salphen)N_3$ [1] with DAD were too rapid to measure by infrared spectroscopy. Extensive dissociation of PPh_3 from all of these complexes occurs and the extent of dissociation is greater for the triazolate complexes than for the azide complexes in each case [1]. The extent of PPh_3 dissociation parallels the donor ability of the chelate system in these $PPh_3Co(Chelate)X$ complexes ($X = N_3$ or triazolate) in the order $(DH)_2 \sim AcAc \sim Salphen < Salen < BAE$. The reduction potentials for these complexes follow the same sequence: $PPh_3Co(DH)_2N_3$ (−1.35 V); $PPh_3Co(AcAc)_2N_3$ (−1.65 V); $PPh_3Co(Salphen)N_3$ (−1.70 V); $PPh_3Co(Salen)N_3$ (−1.85 V); $PPh_3Co(BAE)N_3$ (−1.86 V) where all potentials were measured in CH_2Cl_2 and are given *versus* Fc^+/Fc.

At this point we know the following with regard to the $R_3PCo(AcAc)_2N_3$ cycloaddition reactions with DAD. These reactions are first order, rate = $k[R_3PCo(AcAc)_2N_3]$, and increase with decreasing cobalt phosphorus bond strength. A complicated mechanism could be written for these reactions (see Appendix) similar to that proposed for the $Ar_3PCo(DH)_2N_3$ reactions [2] but the experimental evidence for the involvement of cobalt(II) species is weaker for the $R_3PCo(AcAc)_2N_3$ reactions. Hence, the following is a possible mechanism for these reactions:

$$R_3PCo(AcAc)_2N_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R_3P + Co(AcAc)_2N_3$$

$$Co(AcAc)_2N_3 + DAD \xrightarrow[RDS]{k_2} Co(AcAc)_2\text{triazolate}$$

$$\text{rate} = k_2[Co(AcAc)_2N_3][DAD]$$

and assuming a steady state for $[Co(AcAc)_2N_3]$ gives

$$\text{rate} = \frac{k_1 k_2 [R_3PCo(AcAc)_2N_3][DAD]}{k_2[DAD] + k_{-1}[R_3P]}$$

and if $k_2[DAD] \gg k_{-1}[R_3P]$, which is consistent with no rate retardation in the presence of excess phosphine, the fast reaction rates and the large [DAD] concentration, then rate = $k_1[R_3PCo(AcAc)_2N_3]$ which agrees with the experimental rate law and $k_1 = k_{obs}$.

Intuitively, this mechanism suggests that the weaker the cobalt–phosphorus bond and the easier the phosphine dissociation, the faster the reaction as has been observed experimentally.

Acknowledgements

Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society and to the Deutschen Forschungs Gemeinschaft and Fonds der Chemischen Industrie for financial support.

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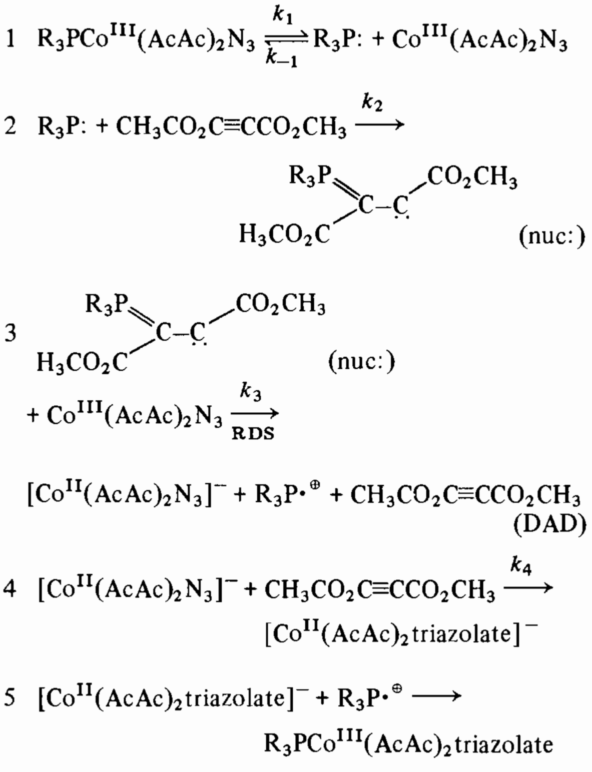
Appendix

Alternative Mechanism for the 1,3-Dipolar Cycloaddition Reactions (Scheme 1)



1 $R_3PCo^{III}(AcAc)_2N_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R_3P: + Co^{III}(AcAc)_2N_3$

2 $R_3P: + CH_3CO_2C{\equiv}CCO_2CH_3 \xrightarrow{k_2}$ (nuc:)

3 (nuc:) $+ Co^{III}(AcAc)_2N_3 \xrightarrow[RDS]{k_3} [Co^{II}(AcAc)_2N_3]^- + R_3P\cdot^{\oplus} + CH_3CO_2C{\equiv}CCO_2CH_3$ (DAD)

4 $[Co^{II}(AcAc)_2N_3]^- + CH_3CO_2C{\equiv}CCO_2CH_3 \xrightarrow{k_4} [Co^{II}(AcAc)_2\text{triazolate}]^-$

5 $[Co^{II}(AcAc)_2\text{triazolate}]^- + R_3P\cdot^{\oplus} \longrightarrow R_3PCo^{III}(AcAc)_2\text{triazolate}$

Scheme 1.

Throughout the course of the reaction, the concentrations of R_3P: and nuc: should remain essentially constant. Assuming a steady state for $[R_3P:]$ and [nuc:] leads to the following expressions for their concentrations:

$$d[R_3P:]/dt = 0 = k_1[R_3PCo^{III}(AcAc)_2N_3] - k_{-1}[R_3P:][Co^{III}(AcAc)_2N_3] - k_2[R_3P:][DAD]$$

$$[R_3P:] = k_1[R_3PCo^{III}(AcAc)_2N_3]/k_{-1} \times [Co^{III}(AcAc)_2N_3] + k_2[DAD]$$

$$d[nuc:]/dt = 0 = k_2[R_3P:][DAD] - k_3[nuc:] \times [Co^{III}(AcAc)_2N_3]$$

$$[nuc:] = k_2[R_3P:][DAD]/k_3[Co^{III}(AcAc)_2N_3]$$

Assuming that step 3 of Scheme 1 is the rate determining step, the derived rate law for the 1,3-dipolar cycloadditions of $LCo(AcAc)_2N_3$ with $CH_3CO_2C{\equiv}CCO_2CH_3$ becomes:

$$\text{Rate} = k_3[nuc:][Co^{III}(AcAc)_2N_3]$$

after substituting the expressions for [nuc:] and $[R_3P:]$ from above

$$\text{Rate} = k_2[R_3P:][DAD] = \frac{k_1k_2[R_3PCo^{III}(AcAc)_2N_3][DAD]}{k_{-1}[Co^{III}(AcAc)_2N_3] + k_2[DAD]}$$

But the kinetics were determined under pseudo-first-order conditions, such that

$$\text{Rate} = k_{obs}[R_3PCo(AcAc)_2N_3]$$

implying that k_{obs} is equal to

$$k_{obs} = \frac{k_1k_2[DAD]}{k_{-1}[Co^{III}(AcAc)_2N_3] + k_2[DAD]}$$

and under the reaction conditions $k_2[DAD] \gg k_{-1}[Co^{III}(AcAc)_2N_3]$

then $k_{obs} = \dfrac{k_1k_2[DAD]}{k_2[DAD]} = k_1$

This equation explains the experimental observations that the rate is essentially independent of [DAD].

There is some justification for the involvement of cobalt(II) species in the reactions of $R_3PCo(AcAc)_2N_3$ with DAD. In the absence of Co(II) species, the reactions should be much slower. For example the following reaction does not involve Co(II) species and is very slow.

$Co_2(AcAc)_4(N_3)_2$ + 10 DAD; $t_{1/2} = 837$ min

and the mechanism of this reaction is probably:

$$[Co_2(AcAc)_4(N_3)_2 \overset{\text{fast}}{\rightleftharpoons} 2[Co(AcAc)_2N_3]$$

$$2Co(AcAc)_2N_3 + 2\,DAD \xrightarrow{\text{slow}} 2[Co(AcAc)_2\text{triazolate}]$$

$Co(AcAc)_2N_3$ reacts with DAD slowly. Thus, dissociation of R_3P from $R_3PCo(AcAc)_2N_3$ should not speed up the reaction enough to explain the results even though the simplified mechanism is consistent with the observed rate law. Thus, the complicated mechanism seems to better explain the observations but we are unable to verify all the steps in it.