

COUPLING OF IMIDOYL CHLORIDES TO DIAZADIENES BY ANIONIC NICKEL COMPLEXES

HOLWARD ALPER *, MASATO TANAKA and (in part) KHALED HACHEM

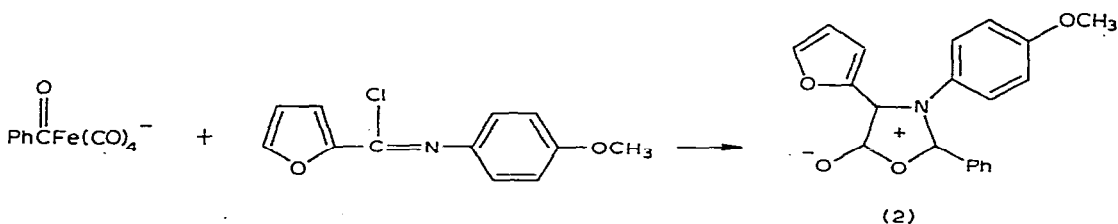
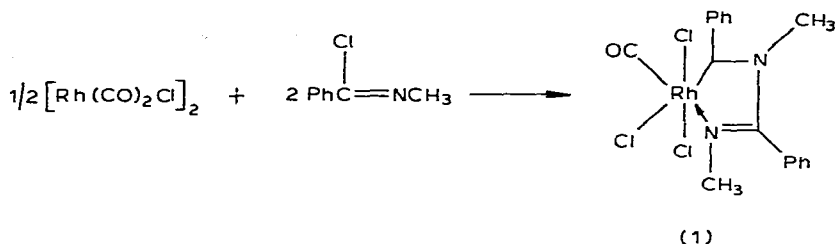
Department of Chemistry, University of Ottawa, Ottawa, Ontario K1N 9B4 (Canada)

(Received August 6th, 1979)

Summary

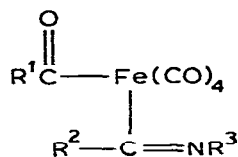
Imidoyl chlorides react with aroyltricarboxynickelates, under mild conditions, to give 1,4-diaza-1,3-butadienes and α -diketones. An electron transfer mechanism is proposed for this reaction.

The reactions of imidoyl chlorides with organometallic complexes has been a particularly active area of research in the past few years [1–7]. Several novel types of organometallic complexes [e.g., 1] have been isolated, [1–6] and mesoionic compounds [e.g., 2] have been synthesized via the remarkable reac-



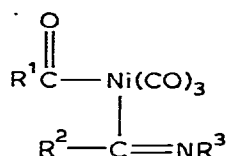
tion of imidoyl halides with acyltetracarbonylferrates [7]. It was proposed that iminoacyliron complexes (3) were initially formed in the latter reaction, and that such complexes then experienced acyl migration rather than reductive eli-

mination (which would have afforded the monoimine derivative of α -diketones).



(3)

Aroyltricarboxylnickelates, usually generated by reaction of organolithium compounds with nickel tetracarbonyl, have been shown to be of some use in organic synthesis [8]. It seemed conceivable to us that reaction of imidoyl chlorides with aroyltricarboxylnickelates would afford 4 (the nickel analog of 3), and

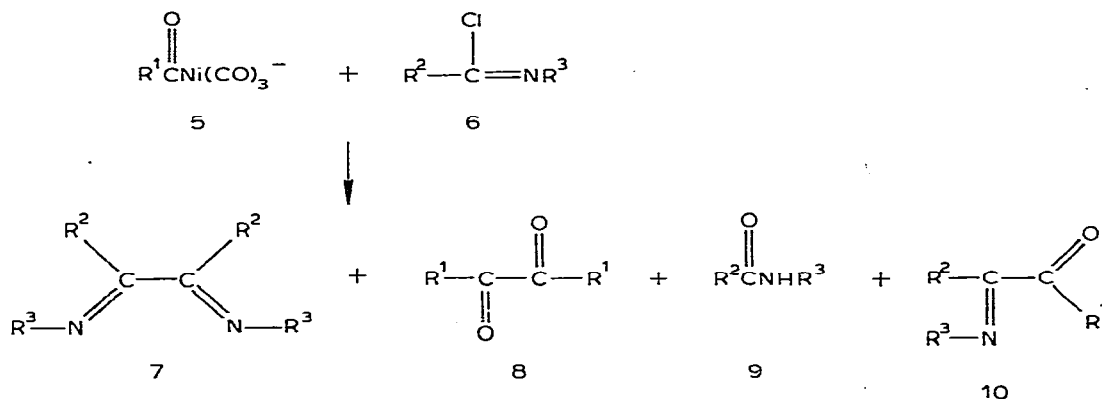


(4)

that the latter may then undergo reductive elimination instead of acyl migration. We now describe the results of a study of this reaction.

Results and discussion

Treatment of benzoyltricarboxylnickelate (5, $\text{R}^1 = \text{Ph}$), generated by reaction of phenyllithium with nickel tetracarbonyl in ether at -60°C , with an equimolar amount of the imidoyl chloride 6 ($\text{R}^2 = p\text{-BrC}_6\text{H}_4$, $\text{R}^3 = \text{Ph}$) first at 0°C and then at room temperature, afforded the 1,4-diaza-1,3-butadiene derivative 7 ($\text{R}^2 = p\text{-BrC}_6\text{H}_4$, $\text{R}^3 = \text{Ph}$) in 28% yield, benzil (8, $\text{R}^1 = \text{Ph}$) in 48% yield, and a small amount (1.6%) of the amide 9 [$\text{R}^2 = p\text{-BrC}_6\text{H}_4$, $\text{R}^3 = \text{Ph}$]. The latter



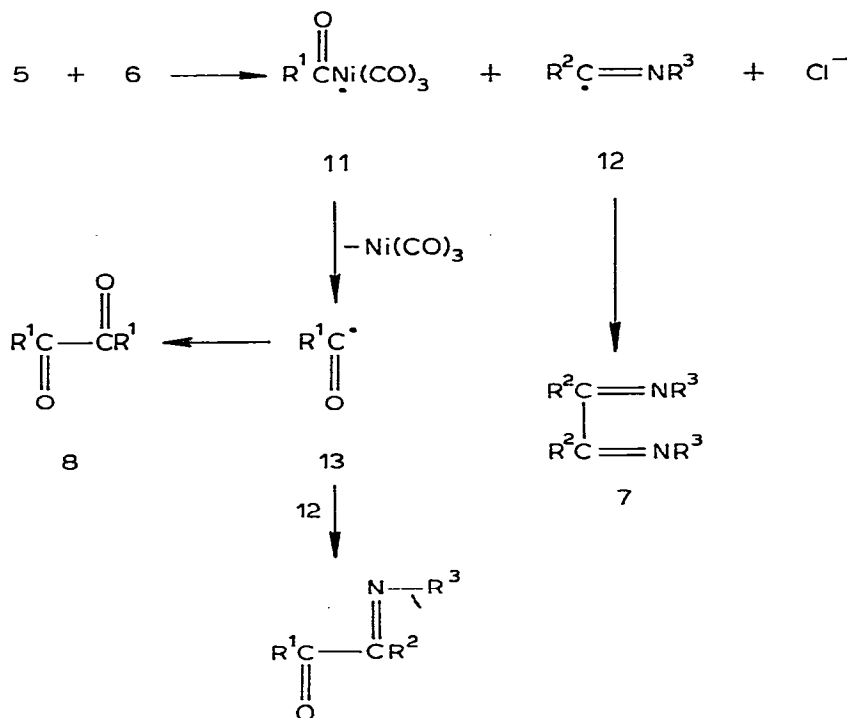
compound results from hydrolysis of unreacted 6 during reaction work-up.

1,4-Diaza-1,3-butadienes [$R^2 = p\text{-CH}_3\text{OC}_6\text{H}_4$, Ph; $R^3 = \text{Ph}$, $p\text{-ClC}_6\text{H}_4$] were obtained in 36–50% yield by reaction of either benzoyl or *p*-toluoyltricarbonylnickelate with several imidoyl chlorides (Table 1). These diazadienes, previously prepared by reaction of α -dicarbonyl compounds with amines, have been widely utilized as ligands in organometallic chemistry [9]. Only in one case [$R^1 = R^2 = R^3 = \text{Ph}$] was the α -diketone monoimine isolated as a by-product in these reactions.

The structures of 7–10 were elucidated on the basis of infrared, nuclear magnetic resonance, and mass spectral data, as well as by elemental analysis. Comparison of melting points and spectral data with authentic samples were also made, where possible.

The results obtained above indicate that complexes of structural type 4 are unlikely intermediates in the reaction (unless 4 was produced, and the subsequent reductive elimination step was slow relative to organic ligand exchange). Rather, they are indicative of an electron transfer pathway (Scheme 1). Such

SCHEME 1



one electron transfer from 5 to 6 would generate the radicals 11 and 12. The diazabutadienes (7) would then arise from selfcoupling of 12, while the benzil species 8 may result from conversion of 11 to the aroyl radical 13, followed by coupling. It is likely that coupling of 12 to give 7 is faster than dissociation of 11 to 13, since one would otherwise anticipate the formation of appreciable amounts of α -diketone monoimine (10).

It is possible that several of the previously reported reactions involving aroyl-

TABLE 1
 PRODUCTS OBTAINED FROM REACTION OF 5 WITH 6

5, R ¹ =; 6, R ² =, R ³ =	Products	Yield (%)	M.p. (°C)	Lit. M.p. (°C)	Anal. found (calc'd)(%)			Pertinent spectral data for new compounds
					C	H	N	
Ph; <i>p</i> -BrC ₆ H ₄ , Ph	7	28	155.5-156.8		60.00 (60.23)	3.37 (3.50)	5.24 (5.40)	IR: $\nu(\text{CN})1621 \text{ cm}^{-1}$ (KBr); NMR: $\delta 6.5-8.0$ ppm (m, 18H, aromatic protons) (CDCl ₃); MS: (m/e)368 [M - 2 Br] ⁺ , 260, 258 [1/2M] ⁺
	8	48	92.0-93.0	95-96 ^a				
	9	1.6	198.5-199.0	197 ^b				
	7	37	144.5-146.0	144 ^c				
Ph; Ph, Ph	8	43						
	10	8	105.0-106.0	106 ^d				
Ph; <i>p</i> -CH ₃ OC ₆ H ₄ , Ph	7	50	151.5-152.0		80.17 (79.98)	5.38 (5.75)	6.65 (6.66)	IR: $\nu(\text{CN})1614 \text{ cm}^{-1}$ (KBr); NMR: $\delta 3.80(6, 6\text{H}, \text{OCH}_3), 6.55-7.60$ ppm (m, 18H, aromatic protons) (CDCl ₃); MS: (m/e)420[M] ⁺
	8	41						
<i>p</i> -CH ₃ C ₆ H ₄ ; Ph; <i>p</i> -ClC ₆ H ₄	9	4.0	165.5-166.5	168 ^b				
	7	36	169.0-171.0		73.11 (72.73)	4.09 (4.22)	6.57 (6.52)	IR: $\nu(\text{CN})1625 \text{ cm}^{-1}$ (KBr); NMR: $\delta 6.5-7.9$ ppm (m, 18H, aromatic protons) (CDCl ₃); MS: (m/e)358 [M - 2 Cl] ⁺ , 216, 214 [1/2M] ⁺
	8	27	102.0-103.0	102 ^e				
	9	7.1	192.0-193.0	192 ^b				

^a Ref. 12, ^b Ref. 13, ^c Ref. 14, ^d Ref. 15, ^e Ref. 16.

tricarbonylnickelates proceed via an electron-transfer mechanism [8]. Clearly, the reaction of imidoyl chlorides with aroyltricarbonylnickelates is fundamentally different than that with aroyl (or aryl) tetracarbonylferrates.

Experimental

General

Melting points were recorded on a Gallenkamp or Fisher-Johns apparatus, and are uncorrected. Elemental analyses were performed by M-H-W Laboratories, Phoenix, Arizona, and by Canadian Microanalytical Service, Ltd., Vancouver, Canada. Infrared spectral determinations were made using Unicam SP1100 spectrometer, equipped with a calibration standard. Varian T60 and MS9 spectrometers were used for ^1H NMR and mass spectral determinations, respectively.

The imidoyl chlorides were prepared by literature methods [10,11] while nickel tetracarbonyl and phenyllithium were commercial reagents. All reactions were run under a dry nitrogen atmosphere.

General procedure for the reaction of imidoyl chlorides with aroyltricarbonylnickelates

To nickel tetracarbonyl (0.50 ml, 3.97 mmol) in ether (3 ml) at -60°C was added 3.9–4.0 mmol of the organolithium reagent. The solution was stirred for 45–60 minutes at -60°C , then at -30°C for 3 hours. After increasing the temperature to 0°C , the imidoyl chloride [3.95–4.00 mmol] in ether [5–10 ml] was added. The solution was stirred overnight at room temperature, filtered, and the filtrate was evaporated. Separation of the products was achieved by preparative thin-layer and/or column chromatography (methylene chloride or chloroform-ether) with the diazadiene (7) being eluted off the column prior to the α -diketone (8) and the amide (9).

Acknowledgement

We are grateful to the Natural Sciences and Engineering Research Council for support of this work.

References

- 1 H. Alper and M. Tanaka, *J. Organometal. Chem.*, 169 (1979) C5.
- 2 M. Tanaka and H. Alper, *J. Organometal. Chem.*, 168 (1979) 97.
- 3 H. Brunner and J. Wachter, *J. Organometal. Chem.*, 155 (1978) C29.
- 4 R.D. Adams, D.L. Chodosh and N.M. Golembeski, *J. Organometal. Chem.*, 139 (1977) C39.
- 5 M.F. Lappert and A.J. Oliver, *J. Chem. Soc. Dalton*, (1974) 65.
- 6 P.B. Hitchcock, M.F. Lappert, G.M. McLaughlin and A.J. Oliver, *J. Chem. Soc. Dalton*, (1974) 68.
- 7 H. Alper and M. Tanaka, *J. Amer. Chem. Soc.*, 101 (1979) 4245.
- 8 R. Noyori, in H. Alper (Ed.), *Transition Metal Organometallics in Organic Synthesis*, Vol. I, Academic Press, New York, 1976, pp. 139–144.
- 9 L.H. Staal, A. Oskam, K. Vrieze, E. Rosendaal and H. Schenk, *Inorg. Chem.*, 18 (1979) 1634, and references cited therein.
- 10 J. v. Braun and W. Pinkernelle, *Chem. Ber.*, 67 (1934) 1218.
- 11 V. Hahn and M. Grdinic, *J. Chem. Eng. Data*, 11 (1966) 211.
- 12 *Handbook of Chemistry and Physics*, 50th ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1969.
- 13 R.L. Shiner, R.C. Fuson and D.Y. Curtin, *The Systematic Identification of Organic Compounds*, 4th ed., John Wiley and Sons, Inc., New York, 1958.
- 14 G. Reddelien, *Chem. Ber.*, 46 (1913) 2723.
- 15 E. Knoevenagel, *J. Prakt. Chem.*, 89 (1914) 1.
- 16 B. Klein, *J. Amer. Chem. Soc.*, 63 (1941) 1474.