Journal of Organometallic Chemistry, 169 (1979) C5—C8

Preliminary communication

SYNTHETIC APPROACHES TO η^1-IMINOACYLCOBALT CARBONYL COMPLEXES

HOWARD ALPER* and MASATO TANAKA

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

(Received January 9th, 1979)

Summary

Reaction of imidoyl chlorides with triphenylphosphinecobalt tricarbonyl anion or with cobalt tetracarbonyl anion in the presence of triphenylphosphine affords η^1-iminoacylcobalt carbonyl complexes in 19—85% yields.

Several recent publications have described the reactions of imidoyl chlorides with metal carbonyl anions. While cyclopentadienyltungsten tricarbonyl anion and the iron dicarbonyl anions form η^1-iminoacyl complexes on reaction with imidoyl chlorides, the cyclopentadienylmolybdenum tricarbonyl anion has been reported to react with PhC(Cl)=NPh and $PhC(Cl){=}NCH_3$ to give, respectively, η^2-iminoacyl complexes [1] and a complex derived from two imidoyl and one anion units [2]. Other examples of η^2-iminoacylmetal carbonyl complexes have been described very recently [3,4].

Adams and coworkers [1] found that imidoyl chloride—metal carbonyl anion reactions were generally rapid (complete in 30 minutes or less). However, the cobalt tetracarbonyl anion—imidoyl chloride reaction proved to be exceptionally slow, requiring approximately two days for completion, and affording a binuclear cobalt complex (I) containing coupled imidoyl fragments. No 1/1 mononuclear complex was formed. This communication describes the first examples of η^1-iminoacylcobalt complexes, prepared by two simple, mild, and convenient methods.

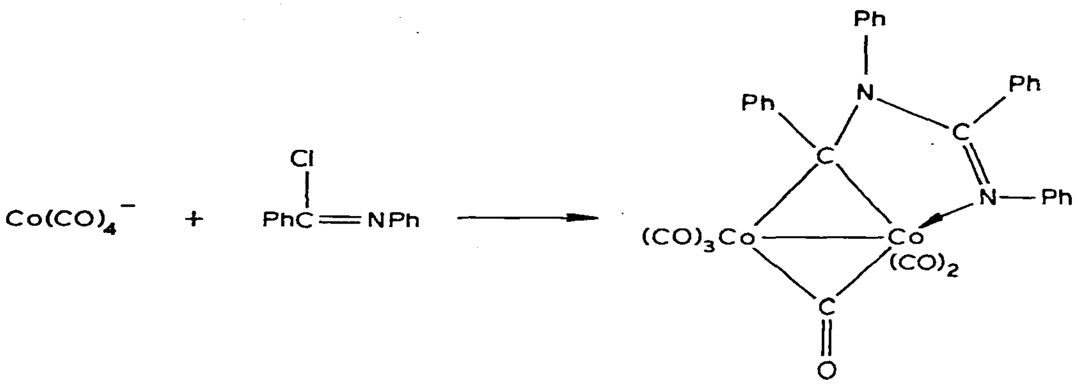
Treatment of a series of imidoyl chlorides (II) with triphenylphosphinecobalt tricarbonyl anion (generated by sodium amalgam reduction of bis(triphenylphosphine)dicobalt hexacarbonyl) in rigorously dry tetrahydrofuran (THF) at 0°C (method A), affords the η^1-iminoacyl complexes (III) in 19—85% yields (Table 1). The latter complexes (III) can also be synthesized by room temperature reaction of the imidoyl halide with the cobalt tetracarbonyl anion in the presence of an equimolar amount of triphenylphosphine (method B). The beautifully crystalline η^1-iminoacylcobalt complexes, identified on the basis of

TABLE 1

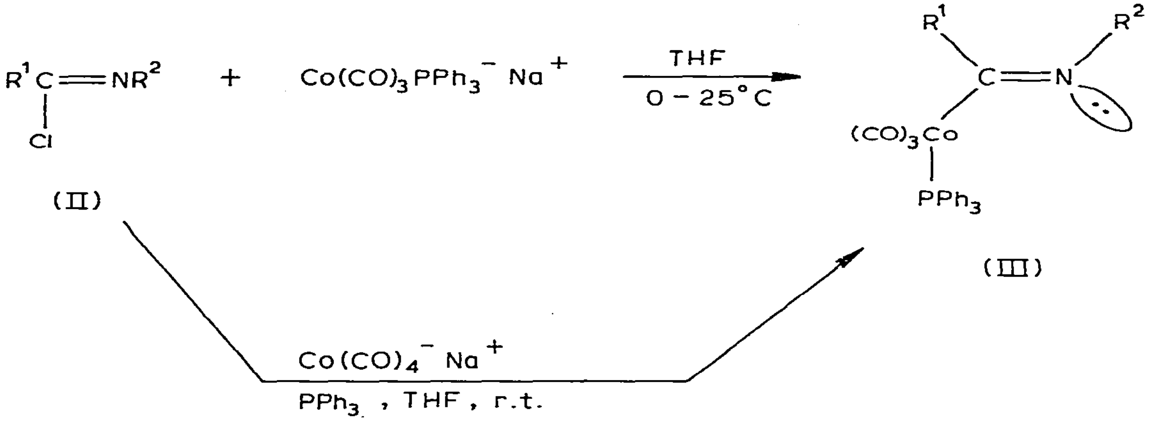
YIELD, ANALYTICAL AND SPECTRAL DATA FOR III

III		Colour[a]	Yield[b] (%)	M.p. (°C) dec.	Anal. (found (calc'd) (%))			IR[c] (cm^{-1})		^1H NMR, δ (ppm)[d]
R^1	R^2				C	H	N	ν(CO)	ν(CN)	
Ph	p-$CH_3C_6H_4$	Y	43(42)	98.5–100.5	70.26 (70.12)	4.34 (4.54)	2.22 (2.34)	2040w 1977s 1960(sh) 1951s	1620m	2.45(s,3H,CH_3), 6.90–7.70(m,24H, aromatic)
p-$CH_3OC_6H_4$	Ph	Y	19[e]	83.0–87.0	68.10 (67.92)	5.46 (5.41)	2.03 (2.03)	2040w 1979s 1971(sh) 1950s	1608m	1.17(t,6H,J 7.0 Hz methyls of solvated ether) 3.50(q,4H,methylenes of solvated ether), 3.82(s,3H,OCH_3) 6.70–7.70(m, 24H,aromatic)
Ph	Ph	YB	44[f]	105.5–108.0	70.01 (69.75)	4.40 (4.30)	2.07 (2.39)	2040w 1977s 1943s	1616m	6.90–7.70(m)
Ph	p-ClC_6H_4	Y	85	99.5–102.0	66.10 (65.87)	3.90 (3.53)	2.31 (2.26)	2040w 1978s 1957s	1612m	6.90–7.60(m)
C_2H_5	Ph	Y	76(78)[g]	100.0–102.5	66.61 (67.05)	4.73 (4.69)	2.22 (2.61)	2038w 1976s 1942s	1625m 1642m	1.33(t,3H,CH_3,J 7.0 Hz), 3.10 (q,2H, CH_2), 6.80–7.60(m,20H,aromatic)
Ph	CH_3	YB	56	115.0–117.0	66.16 (66.55)	4.42 (4.43)	2.25 (2.68)	2035m 1971s 1956(sh) 1948s	1633m	3.73(s,3H,CH_3), 7.10–7.60(m,20H, aromatic)

[a] Y = Yellow, YB = Yellow-brown. [b] Yields given are those obtained using method A. Yields obtained using method B are given in brackets. [c] KBr disc. [d] $CDCl_3$ with tetramethylsilane as internal standard. [e] This complex, after recrystallization from ether/hexane, was solvated by a molecule of ether. [f] Molecular weight: found, 581; calcd., 585.5. [g] Molecular weight: found, 554, calcd., 537.4.



(I)



analytical and spectral data (Table 1), are stable under nitrogen in the solid state, but gradually decompose in solution.

Terminal metal carbonyl stretching bands were observed in the infrared spectra at 2035—2040w, 1971—1979s, and 1942—1957s cm^{-1}, with the carbon nitrogen double bond stretching absorption occurring at 1608—1633 cm^{-1} (KBr disc). The latter absorption occurs in the same region as that for other η^1-iminoacylmetal carbonyl complexes [5]. Proton magnetic resonance spectra are also in accord with the assigned structure. The appearance of only one methyl signal for III, $R^1 = Ph$, $R^2 = CH_3$, and one ethyl pattern for III, $R^1 = C_2H_5$, $R^2 = Ph$, indicates the existence of III in only one stereoisomeric form, i.e., with the lone pair (rather than R^2) *syn* to the very bulky $Co(CO)_3PPh_3$ group.

Molecular ion peaks were not observed in the mass spectra of III. However, vapor phase osmometric molecular weight determinations of III, $R^1 = R^2 = Ph$, and III, $R' = C_2H_5$, $R^2 = Ph$ support the mononuclear nature of these complexes.

The following procedures are representative of each method:

(A) To 1.20 mmol of $PhC(Cl){=}NC_6H_4CH_3$-*p* in THF (5 ml) was added 1.23 mmol of $NaCo(CO)_3PPh_3$ [6] in THF (50 ml) at 0°C. The reaction mixture was allowed to warm to room temperature, and then stirred overnight. The solution was concentrated in vacuo to ca. 10 ml, methylene chloride (10 ml) was added, and then sodium chloride was removed by filtration. Evaporation of the filtrate gave a brown oil which was dissolved in a mixture of methylene chloride (1.0 ml) and ether (5 ml), and then hexane (5 ml) was added. The solution, after filtration to remove small amounts of impurities, was cooled to −45°C to give III, R^1 = Ph, R^2 = *p*-$CH_3C_6H_4$. Yellow mica-like plates (307 mg) of the η^1-iminoacyl complex were obtained on recrystallization from ether (7 ml) and hexane (3 ml).

(B) To a THF solution (7.5 ml) of $NaCo(CO)_4$ (1.27 mmol) was added 0.381 g (1.5 mmol) of PPh_3 and 0.344 g (1.5 mmol) of II, R^1 = Ph, R^2 = *p*-$CH_3C_6H_4$. The reaction mixture was stirred for two days at room temperature, concentrated, and then treated with methylene chloride (5 ml) and ether (5 ml). The solution was filtered, the solid was washed with ether (1 ml) and the washing was added to the filtrate. A brown oil, obtained on filtrate evaporation, was worked-up as described for method A to give 330 mg of analytically pure III, R^1 = Ph, R^2 = *p*-$CH_3C_6H_4$.

Acknowledgment

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

References

1 R.D. Adams, D.F. Chodosh and N.M. Golembeski, J. Organometal. Chem., 139 (1977) C39.
2 H. Brunner and J. Wachter, J. Organometal. Chem., 155 (1978) C29.
3 R.D. Adams and D.F. Chodosh, Inorg. Chem., 17 (1978) 41.
4 W.R. Roper, G.E. Taylor, J.M. Waters and L.J. Wright, J. Organometal. Chem., 157 (1978) C27.
5 R.D. Adams and D.F. Chodosh, J. Amer. Chem. Soc., 99 (1977) 6544.
6 W. Hieber and E. Lindner, Chem. Ber., 94 (1961) 1417.