Reactions of Potassium Carbonyl(π-cyclopentadienyl)nickelate with Butenyl and Cyclopropylmethyl Halides

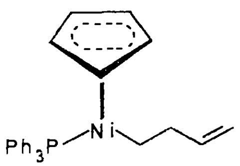
By **John M. Brown,* John A. Conneely,** and **Konstantinos Mertis,** Department of Molecular Sciences, University of Warwick, Coventry CV4 7AL

The reaction of carbonyl(π-cyclopentadienyl)nickel anion with but-3-enyl and cyclopropylmethyl halides has been investigated. In the former case, the only isolated product is 1—3-η-but-2-enyl-π-cyclopentadienylnickel (85:15 (*trans*:*cis*) whereas in the latter, a cyclopropylmethylnickel complex could be isolated. This was converted by thermolysis, or more effectively by photolysis into a 1-σ:4—5-η-1-oxopent-4-enylnickel, most probably derived by insertion of a cyclopropane C–C bond into the metal carbonyl system.

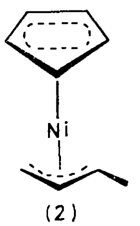
PREVIOUSLY[1] thermolysis and photolysis of but-3-enyl-(π-cyclopentadienyl)triphenylphosphinenickel (1), both leading to 1—3-η-but-2-enyl-π-cyclopentadienylnickel (2) were described. Evidence was presented for the intermediacy of the homoallyl complex (3) in the photoreaction on the basis of deuterium labelling experiments. Since alkyl complexes related to (1) have considerable thermal stability,[2] whilst members of the corresponding carbonyl series [*e.g.* (4a)] are very much more labile[3] with carbon monoxide displacement in (4b) expected to be considerably easier than triphenylphosphine displacement in (1), we examined the synthesis of complexes (4b and c) as possible precursors of (3).

RESULTS AND DISCUSSION

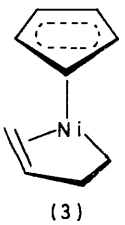
Solutions of carbonylcyclopentadienylnickel anion were generated in tetrahydrofuran by reaction of dimer (5) with sodium–potassium alloy. On reaction with 4-chlorobut-1-ene at —78° the only isolable product was (2) and monitoring of the crude reaction mixture at 0° failed to reveal any i.r. carbonyl stretch which could be associated with a σ-butenyl–carbonyl intermediate. This suggests that carbonyl displacement occurs so readily that (3) [or (6)[1]] is formed and undergoes conversion into (2) sufficiently rapidly to preclude isolation of (4b).



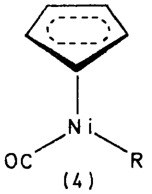
(1)



(2)

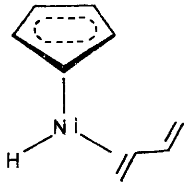


(3)



(4)

a;R = Me
b;R = CH$_2$CH$_2$CH=CH$_2$
c;R = ▷—CH$_2$



(6)

In contrast, reaction of cyclopropylmethyl bromide under the same conditions allowed isolation of an air-sensitive cyclopropylmethyl complex (4c) of moderate stability analogous to previously reported tricarbonyl-π-cyclopentadienylmolybdenum[4] and dicarbonyl-π-cyclopentadienyliron[5] complexes whose i.r. (2015 and 1090 cm^{-1}) and n.m.r. spectra (*cf.* data in Experimental section) demonstrated the integrity of the cyclopropane ring. In the absence of special reaction pathways one might anticipate that cyclopropylmethyltransition-metal complexes would possess high thermal stability, on account of the 12 kcal mol^{-1} additional strain energy incurred by formation of the β-elimination product methylenecyclopropane.[6] Since the photolysis of σ-allylcarbonylmetal complexes proceeds in a number of cases with decarbonylation and concomitant η-allylmetal formation,[7] it was felt that photolysis of (4c) might likewise proceed by decarbonylation, thereby leading to (3) or its tautomer (7). We found, however, that irradiation of (4c) in benzene solution through Pyrex caused rapid conversion into a new product, itself stable to further photoreaction. Work-up produced a yellow oil, shown to be (8), with a strong acyl carbonyl adsorption at 1690 cm^{-1} and co-ordinated olefin absorption at 1445 cm^{-1}. The presence of a co-ordinated vinyl group was further demonstrated by the ^{1}H n.m.r. spectrum in which the terminal vinyl group appears as two well-defined doublets at δ 3·10 (J_{vic} 8 Hz) and 2·32 (J_{vic} 14 Hz). The methylene group adjacent to carbonyl appears as a broad singlet at δ 1·95, it being apparent that no strong vicinal couplings exist to protons on C(3). This strongly implies that the conformation drawn for (8) with torsional angles of *ca.* 60° is to be preferred over (8′) in which substantial $J_{3,4}$ values would be anticipated.*

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* Most n.m.r. spectra containing the fragment (vinyl)CH$_2$CH$_2$-(acyl) are second-order, and analyses are rare; however, one would anticipate substantial vicinal couplings in all conformations except the cisoid and transoid staggered forms where torsional angles are 60° (J 3 Hz on the basis of a simple Karplus relationship).

[1] J. M. Brown and K. Mertis, *J.C.S. Perkin II*, 1973, 1993.

[2] J. Thomson and M. C. Baird, *Canad. J. Chem.*, 1970, **48**, 3443.

[3] D. W. McBride, E. Dudek, and F. G. A. Stone, *J. Chem. Soc.*, 1964, 1752.

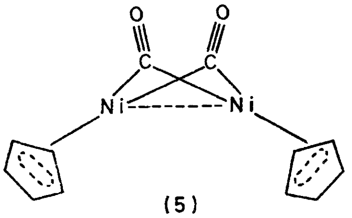
[4] J.-Y. Mérour, C. Charrier, J.-L. Roustan, and J. Benaim, *Compt. rend. C*, 1971, **273**, 285.

[5] W. P. Giering and M. Rosenblum, *J. Amer. Chem. Soc.*, 1971, **93**, 5299.

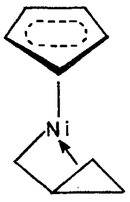
[6] S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, 1969, **69**, 279.

[7] M. L. H. Green and P. L. I. Nagy, *Organometallic Chem. Rev.*, 1964, **2**, 325.

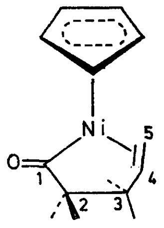
The ^{13}C n.m.r. of (8) shows signals for the terminal vinyl carbons at 48·75 and 83·3 p.p.m., for C(3) at 25·8 p.p.m., and for the methylene carbon atom adjacent to the carbonyl group at 46·7 p.p.m.



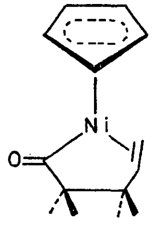
(5)



(7)



(8)

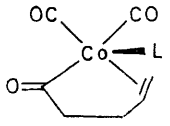


(8′)

Oxopentenyl complexes of this type have been described previously and the tricarbonylcobalt (9a)[8] and carbonyl(π-cyclopentadienyl)iron (10a)[9] derivatives have been prepared, along with the 3,3-dimethyl-1-oxopentenyliron complex (10b). The first-named complex is thermolabile and can only be prepared in solution, but reaction with triphenylphosphine leads to carbonyl displacement and production of (9b), a stable crystalline solid. Complexes (10a and b), however, are quite tractable and in this sense (8) is analogous, being more stable than its alkyl precursor (4c).

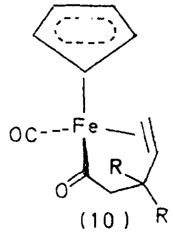
The conversion of (4c) into (8) could proceed by carbonyl photodissociation to form (3) or (7) or alternatively by a pathway in which carbonyl–metal bond cleavage does not occur. In order to distinguish between these, a film of (4c) maintained under high vacuum at room temperature was photolysed when (8) was again produced rapidly, and as the only volatile product. If only 16-electron and 18-electron intermediates[10] are considered, the simplest mechanism is that indicated [(11)] in which carbonyl insertion into the cyclopropane and co-ordination of the incipient olefin occur synchronously. This observation added to the range of examples[11-15] of carbonyl complexes in which an internal strained ring cleavage occurs during complex formation, or subsequently {*e.g.* reaction of bullvalene and other vinylcyclopropanes with enneacarbonyldi-iron where the dominant course of the reaction is metal, or acylmetal insertion into the cyclopropane ring as in the formation of (12) from bicyclo[3.1.0]hex-2-ene[14]}.

It is evident from the 220 MHz spectrum of (4c) that traces of (8) are present and this suggests the possibility of a thermal conversion. When samples of (4c) were maintained at 45° in [^{2}H$_6$]benzene under nitrogen a rather complex decomposition ensued over several hours. In a subsequent preparation of (4c), however, in which the chromatography on alumina was omitted and distillation was carried out at 0·1 mmHg with the bath temperature rising from 60 to 100° during its course, then (8) was obtained pure. This implies that although the activation step must be different in the thermal and photochemical processes, the mechanism must again be associative rather than one which involves carbonyl dissociation–recombination.



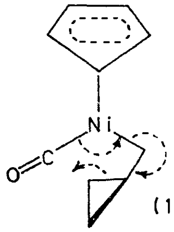
(9)

a; L = CO
b; L = PPh$_3$

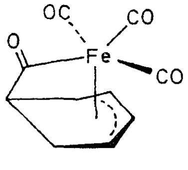


(10)

a; R = H
b; R = Me



(11)



(12)

EXPERIMENTAL

All operations were carried out under nitrogen by Schlenck tube techniques with rigorous exclusion of air.

Reaction of Carbonylcyclopentadienylnickel Anion with Butenyl Chloride.—Bis(carbonyl-π-cyclopentadienylnickel) (3·04 g, 10 mmol) in dry degassed tetrahydrofuran (30 ml) was treated under nitrogen with sodium–potassium alloy (1 : 4 eutectic mixture; 0·82 g, 20 mg atom based on potassium) with stirring and occasional shaking. After 15 min the initial crimson colour had given way to a deep orange-red, and the anion solution was filtered with rigorous exclusion of air and then cooled to −75°. But-3-enyl chloride (1·62 g, 20 mmol) in dry tetrahydrofuran (5 ml) was added slowly over 15 min. The mixture was kept at −75° for 1 h and then warmed slowly to room temperature and stirred for a further 2 h. The solvent was removed *in vacuo* and the product extracted with n-pentane, the extract being chromatographed on basic alumina (50 g). A red-purple band was eluted which after removal of solvent and short-path distillation (10^{-3} mmHg) was demonstrated to be 1—3-η-but-2-enyl-π-cyclopentadienylnickel (85 *trans* : 15 *cis*)

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[8] R. F. Heck and D. S. Breslow, *J. Amer. Chem. Soc.*, 1961, **83**, 1097.

[9] M. L. H. Green and M. J. Smith, *J. Chem. Soc.* (*A*), 1971, 3220.

[10] C. A. Tolman, *Chem. Soc. Rev.*, 1972, 337.

[11] M. I. Bruce, M. Z. Iqbal, and F. G. A. Stone, *J. Organometallic Chem.*, 1969, **20**, 161.

[12] P. J. van Vuuren, R. J. Fletterick, J. Meinwald, and R. E. Hughes, *J. Amer. Chem. Soc.*, 1971, **93**, 4394.

[13] C. B. Reese and A. Shaw, *Chem. Comm.*, 1970, 1365.

[14] R. Aumann, *Angew. Chem. Internat. Edn.*, 1971, **10**, 188, 189, 190; *J. Organometallic Chem.*, 1973, **47**, C29; A. Eisenstadt, *Tetrahedron Letters*, 1972, 2005; R. M. Moriarty, C.-L. Yeh, and K. C. Ramey, *J. Amer. Chem. Soc.*, 1971, **93**, 6709.

[15] S. Sarel, R. Ben-Shoshan, and B. Kirson, *Israel J. Chem.*, 1972, **10**, 787; R. Victor, R. Ben-Shoshan, and S. Sarel, *Tetrahedron Letters*, 1970, 4253.

with no evidence for any σ-butenylnickel products (60 MHz n.m.r.).

Reaction of Carbonylcyclopentadienylnickel Anion with Cyclopropylmethyl Bromide.—The anion, prepared as above on the same scale, was treated with cyclopropylmethyl bromide (2·7 g, 20 mmol) in tetrahydrofuran (5 ml). Work-up, chromatography, and distillation as before gave a very air-sensitive red oil, shown to be carbonyl(π-cyclopentadienyl)cyclopropylmethylnickel (4c) (400 mg, *ca.* 10%), $\nu_{max.}$ (C_6H_6) 2920m, 2890m, 2810m, 2015vs, 1090s, and 800m cm^{-1}, δ (C_6D_6) 5·05 (5H, s, C_5H_5), 1·65 (2H, d, $J_{1,2}$ 7 Hz, $NiCH_2$), 0·90 (1H, m), 0·55 (2H, dt, *trans*-H_2), and 0·15 (2H, dt, *cis*-H_2).

Photolysis of Complex (4c).—(a) A solution of complex (4c) (150 mg) in [$^2H_6$]benzene (0·5 ml) was irradiated (Hanovia black-light lamp; 100 W) through Pyrex for 2 h, when the initial deep red colour had changed to orange. No evolution of gas was observed. The resulting solution was chromatographed on neutral alumina, and a yellow band eluted with n-pentane. Removal of solvent, and molecular distillation gave π-cyclopentadienyl-1-σ : 4—5-η-1-oxopent-4-enylnickel (8), *m/e* 206, 178, 123, 65, and 58, $\nu_{max.}$ (C_6H_6) 2920br, 1690vs, 1445s, 1230w, 1060w, 955w, and 785s cm^{-1} δ (C_6D_6) 5·25 (6H, s, C_5H_5, obscuring 4-H), 3·10 (1H, d, $J_{4,cis\text{-}5}$ 8 Hz, *cis*-5-H), 2·32 (1H, d, $J_{4,trans\text{-}5}$ 14 Hz, *trans*-5-H), 1·95br (2H, s, 2-H_2), and 1·35 (2H, m, 3-H_2), ^{13}C n.m.r. (C_6D_6; 22·63 MHz; {^1H}) 94·3 (C_5H_5), 48·75 (C-5) 83·3 (C-4), 25·8 (C-3), and 46·7 p.p.m. (C-2). Under the pulse conditions employed C-1 and C≡O were not observed.

(b) A solution of complex (4c) (150 mg) in benzene (1 ml) was transferred to the photolysis apparatus and solvent removed *in vacuo*. The resulting deep red film was irradiated as before for 30 min, whilst a pressure of 0·01 mmHg was maintained. Addition of dry ice–acetone to the cold-finger and decreasing the pressure by switching in a mercury diffusion pump caused distillation of a yellow oil, shown to be identical with (8).

Direct Preparation of Complex (8).—A solution of the anion [from dimer (s) (3·04 g)] was prepared as before and treated with cyclopropylmethyl iodide in tetrahydrofuran. Direct distillation of the mixture at 0·1 mmHg (bath temperature 60—100°) gave an orange oil, identical with (8).

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