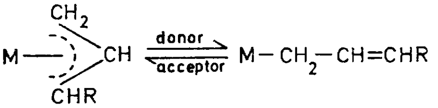
(1—3-η-Allyl)dicarbonylnitrosyliron Complexes and their σ-, 1-σ,2—3-η-, and 1—3-η-Allyl and But-3-enoyl Derivatives with Phosphine Ligands

By **Giuseppe Cardaci,*** Institute of Physical Chemistry, University of Perugia, 06100 Perugia, Italy
Antonio Foffani, Institute ' G. Ciamician,' University of Bologna, 40126 Bologna, Italy

The 1—3-η-allyl complexes $[(\eta\text{-}C_3H_4X)Fe(CO)_2NO]$ [I; X = H, 1-Me, -Cl, -CN, -Ph, or -(Cl, Me), and 2-Me, -Cl, or -Br] react with phosphine ligands [L = PBu^n_3, PPh_2Et, PPh_3, $P(OMe)_3$, $P(OEt)_3$, $P\{(OCH_2)_3CMe\}$, or $P\{(OCH_2)_3CEt\}$] to give five-co-ordinate complexes, $[(\sigma\text{-}C_3H_4X)Fe(CO)_2(NO)L]$, (III), which then undergo chelation to $[(\sigma,\eta\text{-}C_3H_4X)Fe(CO)(NO)L]$, (IV). When X = H, Me, or Ph, the intermediate complex (III) has not been detected, possibly due to the subsequent process of chelation being too fast. The symmetry of complexes (IV), between 1—3-η- and 1-σ,2—3-η-structures, depends on the substituent X and on the steric hindrance due to the entering ligand L. When L = $P(OR)_3$ (R = Me or Et) and X = Cl or Br, a side process to that of chelation is operative which leads to but-3-enoyl complexes, (V), with insertion of CO between the metal atom and the σ-allyl group. With L = $Ph_2PCH_2CH_2PPh_2$ and X = Cl, Br, or CN, insertion of CO is the predominant reaction.

THERE is increasing interest in the structure and reactivity of allyl complexes of transition metals, due to the potential use of these complexes as homogeneous catalysts. Donor entering ligands in such complexes are generally able [1] to change η-allyl ligands to a σ-structure, while acceptor ligands act in the reverse direction stabilizing the η-structure according to the general equilibrium (1), which may account for the catalytic action of allyl complexes. Equilibria of this kind are also found for carbonyl complexes of transition metals; here, however, the σ- and η-structures, when observed, are remarkably stable and do not give rise, generally, to fast rearrangements between them.[2] For some complexes, insertion of a CO group between a σ-allyl group and the metal atom has been observed.[3]



(1)

Following a preliminary communication,[4] we now report the synthesis and structure of a series of iron carbonyl nitrosyl complexes obtained by reacting η-allyl complexes $[(\eta\text{-}C_3H_4X)Fe(CO)_2NO]$ [I; X = H, 1-Me, -Cl, -CN, -Ph, or -(Cl, Me), and 2-Me, -Cl, or -Br] with phosphine ligands [L = PBu^n_3, PPh_2Et, PPh_3, $P(OMe)_3$, $P(OEt)_3$, $P\{(OCH_2)_3CMe\}$, or $P\{(OCH_2)_3CEt\}$].

EXPERIMENTAL

I.r. spectra were determined using a Perkin-Elmer 257 spectrophotometer, ^1H n.m.r. spectra with a Perkin-Elmer R12B spectrometer using tetramethylsilane as internal standard. All reactions were carried out under a nitrogen atmosphere.

Gas Volumetric Measurements.—The volume of CO evolved during reactions was measured with a thermostatted burette.[5] The complex, sealed in a thin ampoule, was introduced into the reaction flask which already contained a solution of the phosphine ligand. The latter solution was saturated with carbon monoxide and was thermostatted at the reaction temperature. The pressure in the burette was equilibrated and the ampoule was then broken and the reaction completed under magnetic shaking. In some cases reactions were also followed spectrophotometrically.

Preparations.—*η-Allyl complexes* $[(\eta\text{-}C_3H_4X)Fe(CO)_2NO]$, (I). These complexes were prepared by reacting $Na[Fe(CO)_3NO]$ [6] with the required allyl halide [7] in diethyl ether solution which had been dehydrated and deaerated.

Dicarbonyl[1—3-η-(1-*methylallyl*)]*nitrosyliron*. Equimolar amounts of the salt $Na[Fe(CO)_3NO]$ and 3-bromobut-1-ene were allowed to react in diethyl ether for 24 h at room temperature. The red complex was obtained as a liquid by fractional distillation of the solution;[8] yield 62% (Found: C, 36·8; H, 3·75; N, 7·10. Calc. for $C_6H_7FeNO_3$: C, 36·5; H, 3·60; N, 7·10%). This complex has been described previously.[7a]

Dicarbonyl[1—3-η-(2-*methylallyl*)]*nitrosyliron*. Equimolar amounts of the salt $Na[Fe(CO)_3NO]$ and 3-chloro-2-methylpropene were allowed to react as previously indicated. The red *complex* was purified as before; yield 55% (Found: C, 36·3; H, 3·40; N, 7·35. Calc. for $C_6H_7FeNO_3$: C, 36·6; H, 3·60; N, 7·10%).

Dicarbonyl[1—3-η-(1-*chloroallyl*)]*nitrosyliron*. Equimolar amounts of the salt $Na[Fe(CO)_3NO]$ and *cis,trans*-1,3-dichloropropene were allowed to react for 5 h in diethyl ether solution. The red liquid *complex* was purified as before; yield 50% (Found: C, 27·2; H, 1·95; N, 6·70. Calc. for $C_5H_4ClFeNO_3$: C, 27·65; H, 1·85; N, 6·45%).

Dicarbonyl[1—3-η-(2-*chloroallyl*)]*nitrosyliron*. Equimolar amounts of the salt $Na[Fe(CO)_3NO]$ and 2,3-dichloropropene were allowed to react for 3 h in diethyl ether solution. The red liquid *complex* was purified as before; yield 55% (Found: C, 27·5; H, 1·75; N, 6·25. Calc. for $C_5H_4ClFeNO_3$: C, 27·65; H, 1·85; N, 6·45%).

[1—3-η-(2-*Bromoallyl*)]*dicarbonylnitrosyliron*. Equimolar amounts of the salt $Na[Fe(CO)_3NO]$ and 2,3-dibromopropene were allowed to react for 0·5 h in diethyl ether solution. The deep red liquid *complex* was purified as

---

[1] G. Henrici-Olivé and S. Olivé, *Angew. Chem. Internat. Edn.*, 1971, **10**, 105; W. Brenner, P. Heinbach, H. Hey, F. W. Muller, and G. Wilke, *Annalen*, 1969, **727**, 161; M. Tsutsui, M. Hancock, J. Ariyoshi, and M. N. Levy, *Angew. Chem. Internat. Edn.*, 1969, **8**, 410.

[2] W. R. McClellan, H. H. Hoehn, M. N. Cripps, E. L. Muetterties, and B. W. Howk, *J. Amer. Chem. Soc.*, 1961, **83**, 1601; M. Cousins and M. L. H. Green, *J. Chem. Soc.*, 1963, 889; M. L. H. Green and P. L. I. Nagy, *ibid.*, p. 189; M. L. H. Green and A. N. Staar, *J. Organometallic Chem.*, 1963, **1**, 230.

[3] R. F. Heck, *J. Amer. Chem. Soc.*, 1963, **85**, 655, 657.

[4] G. Cardaci, S. M. Murgia, and A. Foffani, *J. Organometallic Chem.*, 1972, **37**, C11.

[5] F. Calderazzo and F. A. Cotton, *Inorg. Chem.*, 1962, **1**, 30; G. Innorta, G. Reichenbach, and A. Foffani, *J. Organometallic Chem.*, 1970, **22**, 731.

[6] W. Hieber and H. Beutner, *Z. anorg. Chem.*, 1962, **320**, 101.

[7] (*a*) H. D. Murdoch, *Z. Naturforsch.*, 1965, **B20**, 179; (*b*) R. Bruce, F. M. Chaudari, G. R. Knox, and P. L. Pauson, *ibid.*, p. 73; (*c*) F. M. Chaudari, G. R. Knox, and P. L. Pauson, *J. Chem. Soc.* (*C*), 1967, 2255.

[8] G. Cardaci and S. M. Murgia, *J. Organometallic Chem.*, 1970, **25**, 483.

before; yield 40% (Found: C, 22·7; H, 1·45; N, 5·15. Calc. for $C_5H_4BrFeNO_3$: C, 22·95; H, 1·60; C, 5·35%).

Dicarbonyl[1-3-η-(*cyanoallyl*)]*nitrosyliron*. Equimolar amounts of the salt $Na[Fe(CO)_3NO]$ and *cis,trans*-3-bromo-1-cyanopropene, prepared following ref. 9, were allowed to react for 10 min in diethyl ether solution. This complex could not be purified by fractional distillation.

Dicarbonylnitrosyl[1—3-η-(1-*phenylallyl*)]*iron*. Equimolar amounts of the salt $Na[Fe(CO)_3NO]$ and 3-bromo-1-phenylpropene were allowed to react in diethyl ether solution for 0·5 h. This complex was not purified by fractional distillation; gas-chromatographic purification was not possible because the complex was decomposed.

Dicarbonyl[1—3-η-(1-*chloro*-1-*methylallyl*)]*nitrosyliron*. Equimolar amounts of the salt $Na[Fe(CO)_3NO]$ and *cis,trans*-1,3-dichlorobut-2-ene were allowed to react in diethyl ether solution for 10 h. The red complex gave poor analyses for the allyl ligand.

η-*Allyl complexes* $[(\eta\text{-}C_3H_4X)Fe(CO)(NO)L]$, (II).

Carbonyl[1—3-η-(2-*methylallyl*)]*nitrosyl*(*triphenylphosphine*)*iron*. Equimolar amounts of complex (I; X = 2-Me) and PPh_3 were allowed to react in toluene solution at 50 °C for 24 h. One mole of CO per mole of complex was evolved. The resulting solution was desiccated and the red solid *complex* was crystallized from dichloromethane–n-pentane, m.p. 158—160 °C; yield 85% (Found: C, 63·8; H, 5·70; N, 3·65. Calc. for $C_{23}H_{22}FeNO_2P$: C, 64·05; H, 5·40; N, 3·25%).

Carbonyl[1—3-η-(1-*methylallyl*)]*nitrosyl*(*triphenylphosphine*)*iron*. Equimolar amounts of complex (I; X = 1-Me) and PPh_3 were allowed to react in toluene solution at 50 °C for 20 h. The red solid *complex* was purified as above, m.p. 116—118 °C, yield 70% (Found: C, 63·7; H, 5·00; N, 3·10. Calc. for $C_{23}H_{22}FeNO_2P$: C, 64·05; H, 5·40; N, 3·25%).

Carbonyl[1—3-η-(2-*methylallyl*)]*nitrosyl*(*triethyl phosphite*)*iron*. Equimolar amounts of complex (I; X = 2-Me) and $P(OEt)_3$ were allowed to react at 30 °C for 12 h. The resulting solution was desiccated and the liquid residue was chromatographed over Al_2O_3, eluting with dichloromethane–n-pentane (1 : 2). The product was obtained as a red liquid after evaporation of the solvent. It was not possible by chromatography to remove the ligand entirely.

All complexes (II) did not give $[(\eta\text{-}C_3H_4X)Fe(NO)L_2]$ even under drastic conditions (90 °C, 80 h), as observed for $[(\eta\text{-}C_3H_5)Fe(CO)_2(NO)L]$.[8]

σ-*Allyl complexes* $[(\sigma\text{-}C_3H_4X)Fe(CO)_2(NO)L]$, (III).

Dicarbonyl[σ-(2-*chloroallyl*)]*nitrosyl*(*triphenylphosphine*)-*iron*. Complex (I; X = 2-Cl) and PPh_3 (1 : 2 molar ratio) were allowed to react in benzene solution at 25 °C for 24 h. The resulting solution was quickly evaporated and the *residue* crystallized at −15 °C from dichloromethane–n-pentane, m.p. 97 ± 1 °C; yield 40% (Found: C, 57·4; H, 4·10; Cl, 7·70; N, 3·15. Calc. for $C_{23}H_{19}ClFeNO_3P$: C, 57·6; H, 4·0; Cl, 7·40; N, 4·10%).

Dicarbonyl[σ-(2-*chloroallyl*)](4-*methyl*-2,6,7-*trioxa*-1-*phosphabicyclo*[2.2.2]*octane*)*nitrosyliron*. Complex (I; X = 2-Cl) and $P\{(OCH_2)_3CMe\}$, prepared as described in ref. 10, (1 : 4 molar ratio) were allowed to react in benzene solution for 5 h at 25 °C. Complete purification of the red solid complex was not possible owing to fast subsequent reaction.

Dicarbonyl[σ-(3-*chloroallyl*)]*nitrosyl*(*triphenylphosphine*)-*iron*. Complex (I; X = 1-Cl) and PPh_3 (1 : 10 molar ratio) were allowed to react in benzene solution for 12 h. The resulting solution was evaporated, but purification by crystallization in dichloromethane–n-pentane solution was not possible owing to subsequent reaction.

σ,η-*Allyl complexes* $[(\sigma,\eta\text{-}C_3H_4X)Fe(CO)(NO)L]$, (IV). The σ-allyl complexes (III) react further by CO detachment and chelation to give $[(\sigma,\eta\text{-}C_3H_4X)Fe(CO)(NO)L]$.

Carbonyl[1-σ,2—3-η-(2-*chloroallyl*)]*nitrosyl*(*triphenylphosphine*)*iron*. Equimolar amounts of complex (I; X = 2-Cl) and PPh_3 were allowed to react in toluene solution at 50 °C for 24 h. The red *solid*, obtained after evaporation of the solvent, was purified by crystallization from dichloromethane–n-pentane, m.p. 125 ± 2 °C; yield 75% (Found: C, 58·6; H, 4·35; Cl, 8·25; N, 3·05. Calc. for $C_{22}H_{19}ClFeNO_2P$: C, 58·5; H, 4·25; Cl, 7·85; N, 3·10%).

Carbonyl[1-σ,2—3-η-(1-*chloroallyl*)]*nitrosyl*(*triphenylphosphine*)*iron*. Equimolar amounts of complex (I; X = 1-Cl) and PPh_3 were allowed to react in toluene solution at 50 °C for 24 h. This *complex* was purified as above, m.p. 118 ± 1 °C; yield 70% (Found: C, 58·6; H, 4·60; Cl, 8·5; N, 3·35. Calc. for $C_{22}H_{19}ClFeNO_2P$: C, 58·5; H, 4·25; Cl, 7·85; N, 3·10%).

Carbonyl[1-σ,2—3-η-(2-*chloroallyl*)](4-*methyl*-2,6,7-*trioxa*-1-*phosphabicyclo*[2.2.2.]*octane*)*nitrosyliron*. Equimolar amounts of complex (I; X = 2-Cl) and $P\{(OCH_2)_3CMe\}$ were allowed to react in toluene solution at 25 °C for 4 h. The red solid *complex* was purified as before, m.p. 138—140 °C; yield 80% (Found: C, 32·55; H, 3·50; N, 4·30. Calc. for $C_9H_{13}ClFeNO_5P$: C, 32·25; H, 3·90; N, 4·15%).

Carbonyl[1-σ,2—3-η-(2-*chloroallyl*)](*ethyldiphenylphosphine*)*nitrosyliron*. Equimolar amounts of complex (I; X = 2-Cl) and PPh_2Et were allowed to react in toluene solution at 30 °C for 10 h. The resulting solution was evaporated and the residue was chromatographed using dichloromethane–n-pentane as eluant. The solvent was evaporated and a red liquid *residue* was obtained; yield 70% (Found: C, 54·1; H, 4·95; N, 3·7. Calc. for $C_{18}H_{19}ClFeNO_2P$: C, 53·75; H, 4·75; N, 3·45%).

Carbonyl[1-σ,2—3-η-(1-*chloroallyl*)](*ethyldiphenylphosphine*)*nitrosyliron*. Equimolar amounts of complex (I; X = 1-Cl) and PPh_2Et were allowed to react in toluene solution at 30 °C for 8 h. The red liquid *complex* was purified as before; yield 65% (Found: C, 53·55; H, 4·65; N, 3·25. Calc. for $C_{18}H_{19}ClFeNO_2P$: C, 53·75; H, 4·75; N, 3·45%).

σ-*Allyl complexes with* CO *inserted*, (V). These complexes were obtained mixed with σ,η-allyl complexes of type (IV) when L = $P(OR)_3$(R = Me or Et), but almost exclusively when L = $Ph_2PCH_2CH_2PPh_2$.

Carbonyl(3-*chlorobut*-3-*enoyl*)*nitrosylbis*(*trimethyl phosphite*)*iron*. Complex (I; X = 2-Cl) and $P(OMe)_3$ (molar ratio 1 : 4) were allowed to react in diethyl ether solution at 30 °C for 1 h. The resulting solution was evaporated. The red liquid residue was chromatographed on Al_2O_3 but the σ-complex was decomposed owing to its instability.

Carbonyl(3-*chlorobut*-3-*enoyl*)*nitrosylbis*(*triethyl phosphite*)-*iron*. Complex (I; X = 2-Cl) and $P(OEt)_3$ (molar ratio 1 : 4) were allowed to react in diethyl ether solution at 30 °C for 1·5 h. The resulting solution was treated as above but the σ-complex also decomposed during chromatography.

[1,2-*Bis*(*diphenylphosphino*)*ethane*]*carbonyl*(3-*chlorobut*-3-*enoyl*)*nitrosyliron*. Equimolar amounts of complex (I; X = 2-Cl) and $Ph_2PCH_2CH_2PPh_2$ were allowed to react in benzene solution at 25 °C for 4 h. The final solution was

---

[9] J. W. E. Glattfield and E. Rietz, *J. Amer. Chem. Soc.*, 1940, **62**, 974.

[10] J. G. Verkade and L. T. Reynolds, *J. Org. Chem.*, 1960, **25**, 663.

TABLE 1

CO and NO I.r. stretching bands (cm^{-1}) (toluene solution)

Complex	ν_{CO}	ν_{NO}	Other bands
(I; X = H)	2 034, 1 975	1 745	ν_{CCC} (asym) 1 492 [a]
(I; X = I-Me)	2 029, 1 969	1 743	ν_{CCC} (asym) 1 495 [a]
(I; X = 2-Me)	2 030, 1 969	1 741	ν_{CCC} (asym) 1 490 [a]
(I; X = I-Cl)	2 040, 1 985	1 755	ν_{CCC} (asym) 1 477 [a]
(I; X = 2-Cl)	2 044, 1 990	1·753	ν_{CCC} (asym) 1 466 [a]
(I; X = 2-Br)	2 040, 1 982	1 748	ν_{CCC} (asym) 1 460 [a]
(I; X = 1-CN)	2 050, 1 994	1 763	
(I; X = 1-Ph)	2 030, 1 970	1 744	
(I; X = 1-Cl, Me)	2 036, 1 982	1 754	
(II; X = 2-Me, L = PPh_3)	1 924	1 688	
(II; X = 1-Me, L = PPh_3)	1 926	1 690	
[II; X = 2-Me, L = $P(OMe)_3$]	1 930	1 691	
(III; X = 3-Cl, L = PPh_2Et)	2 008, 1 932	1 730	
(III; X = 3-Cl, L = $PBu^n{}_3$)	2 006, 1 899	1 715	
[III; X = 3-Cl, L = $P(OEt)_3$]	2 025, 1 960	1 748	
(III; X = 3-Cl, L = $P(OMe)_3$] [b]	2 025, 1 965	1 750	
(III; X = 3-Cl, L = PPh_3)	2 012, 1 942	1 738	
[III; X = 3-Cl, L = $P\{(OCH_2)_3CEt\}$]	2 037, 1 978	1 749	
(III; X = 2-Cl, L = PPh_2Et)	2 013, 1 942	1 736	
(III; X = 2-Cl, L = $PBu^n{}_3$)	2 009, 1 892	1 721	
[III; X = 2-Cl, L = $P(OEt)_3$]	2 030, 1 962	1 746	
[III; X = 2-Cl, L = $P(OMe)_3$]	2 030, 1 964	1 748	
(III; X = 2-Cl, L = PPh_3)	2 021, 1 952	1 750	
[III; X = 2-Cl, L = $P\{(OCH_2)_3CMe\}$]	2 036, 1 969	1 763	
[III; X = 2-Cl, L = $P\{(OCH_2)_3CEt\}$]	2 035, 1 968	1 763	
[III; X = 2-Br, L = $P(OEt)_3$]	2 033, 1 953	1 740	
(III; X = 3-CN, L = PPh_3)	2 025, 1 945	1 740	
[III; X = 3-CN, L = $P(OEt)_3$]	2 027, 1 960	1 742	
[III; X = 1-Cl, Me, L = $P(OEt)_3$]	2 023, 1 955	1 742	
(IV; X = 2-Cl, L = PPh_3)	1 950	1 708	
[IV; X = 2-Cl, L = $P\{(OCH_2)_3CMe\}$]	1 968	1 725	
(IV; X = 2-Cl, L = PPh_2Et)	1 930	1 697	
(IV; X = 2-Cl, L = $PBu^n{}_3$)	1 892	1 669	
[IV; X = 2-Cl, L = $P(OEt)_3$]	1 950	1 713	
[IV; X = 2-Cl, L = $P(OMe)_3$]	1 952	1 714	
[IV; X = 2-Cl, L = $P\{(OCH_2)_3CEt\}$]	1 965	1 720	
(IV; X = 1-Cl, L = PPh_3)	1 942	1 723	
(IV; X = 1-Cl, L = PPh_2Et)	1 933	1 706	
(IV; X = 1-Cl, L = $PBu^n{}_3$)	1 899	1 667	
[IV; X = 1-Cl, L = $P(OEt)_3$]	1 955	1 714	
[IV; X = 1-Cl, L = $P(OMe)_3$]	1 953	1 713	
[IV; X = 1-Cl, L = $P\{(OCH_2)_3CEt\}$]	1 970	1 725	
[IV; X = 2-Br, L = $P(OEt)_3$]	1 942	1 713	
(IV; X = 1-CN, L = PPh_3)	1 942	1 715	
[IV; X = 1-CN, L = $P(OEt)_3$]	1 947	1 718	
[IV; X = 1-Cl, Me, L = $P(OEt)_3$]	1 955	1·716	
[V; X = 3-Cl, L = $P(OMe)_3$]	1 965	1 716	ν_{CO} (inserted) 1 648
[V; X = 3-Cl, L = $P(OEt)_3$]	1 952	1 715	ν_{CO} (inserted) 1 645
(V; X = 3-Cl, L = $Ph_2PCH_2CH_2PPh_2$) [c]	1 932	1 708	ν_{CO} (inserted) 1 627
(V; X = 4-Cl, L = $Ph_2PCH_2CH_2PPh_2$) [c]	1 933	1 708	ν_{CO} (inserted) 1 639
			$\nu_{C=C}$ 1 625
(V; X = 3-Br, L = $Ph_2PCH_2CH_2PPh_2$) [c]	1 930	1 707	ν_{CO} (inserted) 1 622
(V; X = 4-CN, L = $Ph_2PCH_2CH_2PPh_2$) [c]	1 930	1 703	ν_{CO} (inserted) 1·605

[a] Pure liquid. [b] CS_2 Solvent. [c] CH_2Cl_2 Solvent.

evaporated and the solid residue was purified by slow crystallization (to avoid possible separation as liquid) from dichloromethane–n-pentane. Red-orange *crystals* were obtained, m.p. 177—179 °C; yield 62% (Found: C, 60·35; H, 4·75; Cl, 5·65; N, 2·10. Calc. for $C_{31}H_{28}ClFeNO_3P_2$: C, 60·45; H, 4·55; Cl, 5·75; N, 2·25%).

[1,2-*Bis*(*diphenylphosphino*)*ethane*]*carbonyl*(4-*chlorobut*-3-*enoyl*)*nitrosyliron*. Equimolar amounts of complex (I; X = 1-Cl) and $Ph_2PCH_2CH_2PPh_2$ were allowed to react in benzene solution at 25 °C for 5 h. The red-orange solid *complex* was purified as above, m.p. 165—166 °C; yield 55% (Found: C, 60·75; H, 4·60; N, 2·10. Calc. for $C_{31}H_{28}ClFeNO_3P_2$: C, 60·45; H, 4·55; N, 2·25%).

[1,2-*Bis*(*diphenylphosphino*)*ethane*](3-*bromobut*-3-*enoyl*)-*carbonylnitrosyliron*. Equimolar amounts of complex (I; X = 2-Br) and $Ph_2PCH_2CH_2PPh_2$ were allowed to react in benzene solution at 25 °C for 2 h. The red-orange solid *complex* was purified as before, m.p. 145—146 °C; yield 60% (Found: C, 56·75; H, 4·60; N, 1·90. Calc. for $C_{31}H_{28}BrFeNO_3P_2$: C, 56·4; H, 4·25; N, 2·10%).

[1,2-*Bis*(*diphenylphosphino*)*ethane*]*carbonyl*(4-*cyanobut*-3-*enoyl*)*nitrosyliron*. This complex was prepared as above, but could not be obtained pure.

RESULTS AND DISCUSSION

η-Allyl Complexes [(η-C_3H_4X)Fe$(CO)_2$NO], (I).—The η-structure of these complexes was confirmed by their i.r. and ^1H n.m.r. spectra.

The complexes showed one NO and two CO stretching bands in the range 1 700—2 100 cm^{-1} (Table 1); no absorption was observed at 1 600—1 640 cm^{-1}, attribut-

TABLE 2

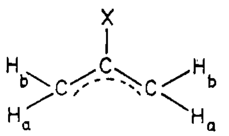
^{1}H N.m.r. spectral data for the complexes

Complex	Solvent	τ	Type of proton	Relative intensity	Multiplicity	J/Hz
(I; X = H) [a]	$CDCl_3$	6·88	H_a	2	2	12
		6·04	H_b	2	2	6
		4·30	H_m	1	7	5
(I; X = 2-Me) [b]	$CDCl_3$	8·40	Me	3	1	
		6·79	H_b	2	1	
		6·00	H_a	2	1	
(I; X = 2-Cl) [b]	$CDCl_3$	6·21	H_b	2	1	
		5·64	H_a	2	1	
(I; X = 2-Br)	CS_2	6·36	H_b	2	1	
		5·78	H_a	2	1	
(I; X = 1-Cl) [c]	CS_2	7·20	H_c		2	11·4
		6·30	H_a		2	7·2
		4·67	H_b		2	8·4
		3·99	H_m		m [f]	6·6
(III; X = 2-Cl, L = PPh_3) [d]	CS_2	6·57	CH_2	2	1	
		5·10	H_a	1	1	
		4·84	H_b	1	1	
(III; X = 2-Cl, L = PPh_2Et) [d]	CS_2	9·03	CH_3 of Et	3	3	7·2
		7·98	CH_2 of Et	2	5	
		6·70	CH_2	2	1	
		5·22	H_a	1	1	
		4·97	H_b	1	1	
(III; X = 3-Cl, L = PPh_3) [e]	CS_2	6·40	CH_2	2	2	6·5
		4·20	H_a, H_b	2	m [f]	
(V; X = 3-Cl, L = $Ph_2PCH_2CH_2PPh_2$) [d]	$CDCl_3$	6·15	CH_2	2	1	
		5·25	H_a	1	1	
		4·92	H_b	1	1	
(V; X = 3-Br, L = $Ph_2PCH_2CH_2PPh_2$) [d]	$CDCl_3$	5·97	CH_2	2	1	
		4·75	H_a	1	1	
		4·61	H_b	1	1	
(V; X = 4-Cl, L = $Ph_2PCH_2CH_2PPh_2$) [e]	$CDCl_3$	6·51	CH_2	2	2	7·2
		4·41	H_a, H_b	2	m [f]	
(II; X = H, L = PPh_3)	$CDCl_3$	7·20			1	
		6·48			m	
(II; X = 2-Me, L = PPh_3)	$CDCl_3$	8·95				
		7·02				
		6·42				
(IV; X = 2-Cl, L = PPh_3)	CS_2	6·75		1		
		6·11		3		
[II; X = 2-Me, L = $P(OEt)_3$] [b]	CS_2	8·49	Me	3	1	
		7·22	H_a	2	1	
		6·43	H_b	2	1	
		8·65	CH_3 of Et	3	3	7·2
		5·96	CH_2 of Et	2	5	

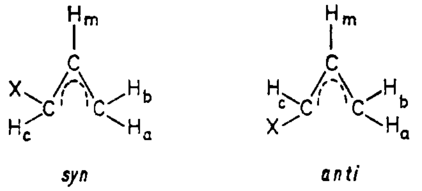
[a] Referred to Scheme 1 (X = H_m). [b] Referred to Scheme 1. [c] Referred to Scheme 2. [d] Referred to structure (A). [e] Referred to structure (B). [f] m = multiplet.

able to C=C stretching, while a band at 1 480—1 510 cm^{-1} was assigned to the ν_{CCC} skeletal stretching mode of the π-bonded allyl group,[11] in agreement with the spectrum of [(η-C_3D_5)Fe(CO)$_2$NO].[12]

Scheme 1 shows that, for complexes in which the allyl group bears a substituent at C(2), two singlets are expected in the ^{1}H n.m.r. spectra, due to the essentially uncoupled protons H_a and H_b.[13] This structure is supported by the data in Table 2. Complexes in which the allyl group bears a substituent at C(1) or C(3) exhibit *syn*- or *anti*-forms[2,11] (Scheme 2). Indeed, complex (I; X = 1-Cl) showed three doublets and a multiplet, as for the corresponding cobalt derivative [(η-C_3H_4X)Co(CO)$_3$],[2] but the data do not allow assignment of the complex to one of the two forms. Contrary to what is observed[2,14] for other 1-methylallyl complexes of cobalt, the present method of preparation does not give a mixture of *syn*- and *anti*-isomers; the n.m.r. spectrum of complex (I; X = 1-Me) corresponded to that reported in ref. 7*a*.



SCHEME 1



SCHEME 2

---

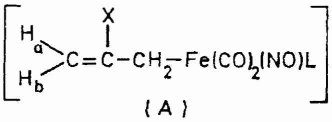
[11] E. J. Lanpher, *J. Amer. Chem. Soc.*, 1957, **79**, 5578.

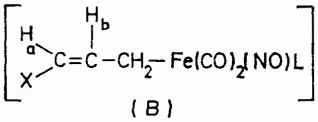
[12] G. Paliani, A. Poletti, G. Cardaci, S. M. Murgia, and R. Cataliotti, *J. Organometallic Chem.*, 1973, **60**, 157.

[13] H. S. Gutowski, M. Karplus, and D. M. Grant, *J. Chem. Phys.*, 1959, **31**, 1278.

[14] J. A. Bertrand, H. D. Jonassen, and D. W. Moore, *Inorg. Chem.*, 1963, **2**, 601.

σ-Allyl Complexes $[(\sigma\text{-}C_3H_4X)Fe(CO)_2(NO)L]$, (III).—Structures (A) and (B) proposed for these complexes are


(A)


(B)

supported by gas-volumetric and spectroscopic (i.r. and n.m.r.) data. Carbon monoxide was not appreciably evolved during the preparation of complexes (III). Two carbonyl stretching bands were still present in the i.r. spectrum (Table 1), indicating that the two CO ligands retain their previous type of bonding; a C=C stretching absorption was observed at 1 590—1 620 cm^{-1}, after purification from excess of ligand, while the skeletal stretching band at 1 500 cm^{-1} disappeared in agreement with a change from π- to σ-bonding of the allyl group.

The structure of the allyl ligand, and the position of the X substituent, in complexes (III) are clarified by the n.m.r. spectra. Complexes obtained from 2-substituted η-allyl derivatives correspond to structure (A). Their spectra (Table 2) showed three groups of absorptions of relative intensities 1 : 1 : 2, attributable to the two terminal protons and to those at the methylene group bonded to the metal atom. The assignments in Table 2 correspond to those given [15] for compounds $CH_2{=}C(Hg){-}CH_3$. Complexes derived from η-allyl ligands bearing substituents at C(1) or C(3) have structure (B), *i.e.* with the X substituent at the terminal position of the allyl chain; this structure has been found in other cases.[1] Only complex (III; X = 3-Cl, L = PPh_3) could be obtained sufficiently pure for a reliable n.m.r. test. It showed (Table 2) two groups of absorptions of the same intensity, of which that at the higher τ value is a doublet attributable to the methylene group bonded to the metal atom and the other is a multiplet (8 bands) in the τ range of ethylenic protons, assigned to the remaining two protons of the allyl chain. A possible structure with the X substituent at the carbon atom bonded to the metal would give rise to two groups of absorptions of relative intensity 3 : 1. The present information does not suffice to elucidate further the stereochemistry of these five-coordinate complexes, particularly as to the relative position of the σ-allyl group and ligand L; this situation is similar to that of analogous complexes of cobalt.[16]

Complexes (II) *and* (IV).—These complexes were obtained by reacting (I) with phosphine ligands. The complexes with X = H, Me, or Ph retain the η-structure, (II), with no evidence for more- or less-stable reaction intermediates. The others undergo reaction *via* intermediate formation of σ-allyl complexes, followed by chelation to give final products, (IV), similar to the η-allyl complexes. N.m.r. evidence (see below) suggests, however, that complexes (IV) have an asymmetrical σ,η-allyl structure as found in other instances [17] and supported by crystal-structure determinations.[18,19] In both cases one mole of carbon monoxide was evolved per mole of reacting complex, and a CO stretching band disappeared in the i.r. spectrum (Table 1).

The structure of the final complexes seems to depend on the steric interaction of the entering ligand L with the X substituent of the allyl group. For instance, the n.m.r. spectrum of complex [II; X = 2-Me, L = $P(OMe)_3$] (Table 2) showed a single pattern corresponding to a symmetrical η-structure (Scheme 1). On the other hand, n.m.r. spectra of complexes (II; X = 2-Me, L = PPh_3) and (IV; X = 2-Cl, L = PPh_3) showed two groups of absorption of relative intensity 1 : 3. This is difficult to explain; it may indicate either the presence of dynamic phenomena or asymmetry of the protons due to partial localization of the double bond as expected for a σ,η-structure. Structures of this kind are theoretically compatible,[20] in that one may consider the metal–allyl bond as resulting from the contribution of two orbitals, one with highest bonding capacity for a 90° angle between the metal–allyl axis and the allyl plane, the other for a 180° angle. The situation of greatest stability would arise for an intermediate angle and would, in fact, correspond to partial localization of the double bond, favoured by the presence of bulky ligands.

σ-Allyl Complexes with CO *inserted*, (V).—These complexes, of structures corresponding to (A) and (B) with CO inserted between the CH_2 group and the iron atom, were identified by gas-volumetric and i.r. information. The volume of carbon monoxide evolved on reacting complex (I; X = 2-Cl) with the ligands $P(OMe)_3$ and $P(OEt)_3$ was *ca.* 40% less than that expected per mole of reacting complex. Moreover, this figure was dependent on ligand concentration. A band at *ca.* 1 650 cm^{-1} (in CS_2) also appeared in the i.r. spectrum (see Table 1), its intensity increasing with ligand concentration. At the same time, the half-width of the CO and NO stretching bands changed remarkably, giving rise to definite shoulders. This suggests the occurrence of a parallel reaction path involving disubstitution and CO insertion in the initially formed σ-bond between the metal atom and the allyl group.

With L = $PPh_2CH_2CH_2PPh_2$, complexes of type (V) were formed exclusively. The structure of these complexes was supported by gas-volumetric, i.r., and n.m.r. data. The absence of CO evolution during the synthesis shows that both CO groups of the starting complexes are still present in the final product. The presence of the bidentate phosphine ligand in the complexes masks i.r. modes in the region below *ca.* 1 600 cm^{-1}, so that discussion is limited to the range 1 600—2 200 cm^{-1} (Table 1). These complexes showed two intense bands at *ca.* 1 930 and 1 700 cm^{-1}, assigned to the CO and NO stretching frequencies. In addition, a band was present

---

[15] D. Moy, M. T. Emerson, and J. P. Oliver, *Inorg. Chem.*, 1963, **2**, 1261.

[16] R. F. Heck, *J. Amer. Chem. Soc.*, 1963, **85**, 651.

[17] J. Powell and B. L. Shaw, *J. Chem. Soc.* (*A*), 1968, 583; 1967, 1839.

[18] R. Mason and D. R. Russell, *Chem. Comm.*, 1966, 26; A. E. Smith, *Acta Cryst.*, 1969, **A25**, S161.

[19] W. E. Oberhansli and L. F. Dahl, *J. Organometallic Chem.*, 1965, **3**, 43; M. R. Churchill and R. Mason, *Nature*, 1964, **204**, 777; R. Seip, *Acta Chem. Scand.*, 1972, **26**, 1966.

[20] S. F. A. Kettle and R. Mason, *J. Organometallic Chem.*, 1966, **5**, 573.

in the range 1 600—1 650 cm^{-1}, the intensity of which was comparable to those above; this band had a marked shoulder in the 4-chlorobut-3-enoyl complex. The intensity and composite structure of this band suggest that it corresponds both to C=C stretching of the σ-allyl group and carbonyl stretching of the CO group inserted between the metal atom and σ-allyl group. The literature shows [7,16] that the range 1 600—1 700 cm^{-1} is that in which the absorptions of inserted CO groups are located. The structure of the allyl group in these complexes was further supported by the n.m.r. spectra (Table 2). The 3-bromo- and 3-chloro-but-3-enoyl complexes showed three bands of relative intensity 1 : 1 : 2. The first two bands correspond to uncoupled [13] olefinic protons, the last to protons of the aliphatic methylene group; therefore the structure corresponds to (A). The 4-chlorobut-3-enoyl complex showed the same pattern as (III; X = 2-Cl, L = PPh_3) and has structure (B). If one assumes that the complex obtained during the first step of the reaction has a σ-allyl structure, then this structure is retained on subsequent CO insertion. Insertion reactions have been extensively studied [21] and it has been shown,[22] for example, that for the complex [$MeMn(CO)_5$] the mechanism of reaction involves alkyl migration rather than CO insertion; for the present reactions the situation may be similar.

We thank the Italian National Research Council for support.

[3/2605 *Received*, 28*th December*, 1973]

---

[21] R. J. Mawby, F. Basolo, and R. Pearson, *J. Amer. Chem. Soc.*, 1964, **86**, 3994; C. S. Kraihanzel and P. K. Marples, *ibid.*, 1965, **87**, 5267; F. Calderazzo and K. Noack, *Co-ordination Chem. Rev.*, 1966, **1**, 118.

[22] K. Noack and F. Calderazzo, *J. Organometallic Chem.*, 1967, **10**, 101.