

## Synthesis and Characterization of New Formamidino and Triazenido Complexes of Rhenium(I): $[\text{Re}(\text{CO})_2(\text{PPh}_3)_2(\text{ArN}\cdots\text{X}\cdots\text{NAr})]$ ( $\text{X} = \text{CH}, \text{N}$ )

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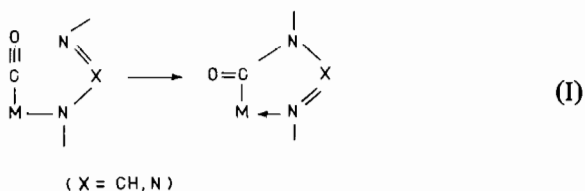
*$[\text{Re}(\text{CO})_3(\text{PPh}_3)_2\text{Cl}]$  reacts with  $\text{Li}(\text{ArN}\cdots\text{X}\cdots\text{NAr})$  ( $\text{X} = \text{CH}, \text{N}$ ;  $\text{Ar} = p\text{-CH}_3\text{C}_6\text{H}_4, \text{C}_6\text{H}_5, p\text{-ClC}_6\text{H}_4, p\text{-FC}_6\text{H}_4$ ) in boiling THF to yield  $[\text{Re}(\text{CO})_2(\text{PPh}_3)_2(\text{ArN}\cdots\text{X}\cdots\text{NAr})]$ . The structure of these new complexes and the mode of coordination of the organonitrogen ligand are discussed on the basis of i.r. and  $^1\text{H n.m.r.}$  spectra.*

### Introduction

The recent interest in the chemistry of complexes containing pseudo-allyl ligands  $[\text{N}(\text{NR})_2]^-$ , triazenido and  $[\text{HC}(\text{NR})_2]^-$ , formamidino, concerns many transition metals and is mainly focused on their synthesis and mode of coordination of the organonitrogen ligand and their reactivity.

It has been shown that these ligands can act as monodentate [1,2], chelate [3–6], bridging [7–12], or orthometalate [13]. In addition, the monodentate ligand may display a fluxional behaviour [1, 2, 14]. Moreover very recently there has been reported a novel Rh–Hg complex containing two formamidino or triazenido groups, one chelating the rhodium atom and the other bridging a rhodium–mercury bond, for which a novel dynamic process has been established consisting of interchange of the bridging and the chelating organonitrogen ligands *via* a monodentate intermediate [15, 16].

Regarding their reactivity of particular interest are those complexes containing also carbonyl groups because they can give rise to carbamoyl complexes, where the carbon atom of the carbamoyl group is the fourth atom in a chelate chain [1, 12, 17, 18], as schematized in (I):



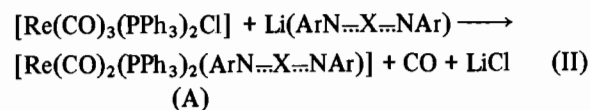
Species of this type may be intermediates in the carbonylation of triazenes  $\text{ArNH-N=NAr}$  to amides  $\text{ArNHCOAr}$  (with loss of nitrogen) promoted by a  $\text{PdCl}_2(\text{PPh}_3)_2$  catalyst precursor [19].

Very recently it has been reported that manganese or rhenium carbonyls  $[\text{M}(\text{CO})_5\text{Cl}]$  ( $\text{M} = \text{Mn}, \text{Re}$ ) react with lithioformamidino giving rise to metal-carbamoyl carbonyl complexes of the type  $[\text{M}(\text{CO})_4\{\text{CO}\text{NArCH}(\text{NAr})\}]$  which upon heating or irradiation are decarbonylated yielding the corresponding metal formamidino carbonyl complexes  $[\text{M}(\text{CO})_4(\text{ArN}\cdots\text{CH}\cdots\text{NAr})]$ ; these latter complexes were directly obtainable starting with  $[\text{M}(\text{CO})_4\text{Cl}]_2$  [20]. By interacting  $[\text{M}(\text{CO})_5\text{Br}]$  with  $\text{Na}(\text{ArN}_3\text{Ar})$   $[\text{M}(\text{CO})_4(\text{ArN}_3\text{Ar})]$  was obtained directly [21]. This complex was obtained also from  $[\text{M}(\text{CO})_5\text{Br}]$  with 1,3-diaryltriazenido-trimethylsilicons and trimethyltins ( $\text{M} = \text{Mn}$ ) [22]. It was found that in the  $[\text{Mn}(\text{CO})_4(\text{ArN}_3\text{Ar})]$ , phosphines and arsines replaced carbon monoxide rather than the triazenido group, and that there was no indication of further incorporation of phosphine or arsine [22].

Investigations in our laboratory on the reactivity of  $[\text{Re}(\text{CO})_3(\text{PPh}_3)_2\text{Cl}]$  with lithio-formamidino or -triazenido have led to the isolation and characterization of new complexes of the type  $[\text{Re}(\text{CO})_2(\text{PPh}_3)_2(\text{ArN}\cdots\text{X}\cdots\text{NAr})]$  ( $\text{X} = \text{CH}, \text{N}$ ) which are discussed hereafter.

### Results and Discussion

The new complexes (A) were obtained in good yields (*ca.* 85%) according to eqn. (II), upon adding  $[\text{Re}(\text{CO})_3(\text{PPh}_3)_2\text{Cl}]$  as a solid to a boiling THF solution of  $\text{Li}(\text{ArN}\cdots\text{X}\cdots\text{NAr})$  generated *in situ* by treating  $\text{ArNHXNAr}$  with  $\text{Li}(n\text{-Bu})$ :



(X = CH, N; Ar =  $p\text{-CH}_3\text{C}_6\text{H}_4, \text{C}_6\text{H}_5, p\text{-ClC}_6\text{H}_4, p\text{-FC}_6\text{H}_4$ ).

TABLE I. Analytical Data.

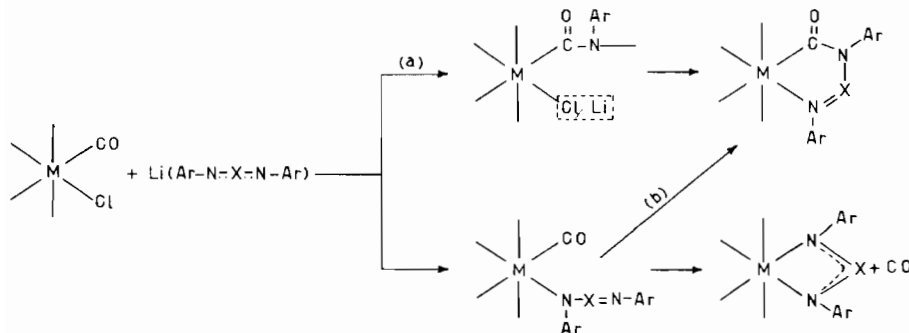
Compound	M. p. (°C)	Colour	Yield (%)	Analysis: Found (Calc.)(%)			
				C	H	N	Cl
I [Re(CO) <sub>2</sub> {CH(NC <sub>6</sub> H <sub>4</sub> p-CH <sub>3</sub> ) <sub>2</sub> }(PPh <sub>3</sub> ) <sub>2</sub> ]·CH <sub>2</sub> Cl <sub>2</sub>	221	yellow	85	60.61 (60.33)	4.37 (4.41)	2.51 (2.60)	5.93 (6.60)
II [Re(CO) <sub>2</sub> {CH(NC <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> }(PPh <sub>3</sub> ) <sub>2</sub> ]·CH <sub>2</sub> Cl <sub>2</sub>	226	yellow	80	59.00 (59.40)	3.83 (4.10)	2.53 (2.67)	6.67 (6.78)
III [Re(CO) <sub>2</sub> {CH(NC <sub>6</sub> H <sub>4</sub> p-Cl) <sub>2</sub> }(PPh <sub>3</sub> ) <sub>2</sub> ]	254	yellow	80	59.06 (59.40)	4.15 (3.81)	2.60 (2.71)	6.80 (6.87)
IV [Re(CO) <sub>2</sub> {CH(NC <sub>6</sub> H <sub>4</sub> p-F) <sub>2</sub> }(PPh <sub>3</sub> ) <sub>2</sub> ]	238	yellow	90	61.69 (61.36)	4.48 (3.94)	2.55 (2.80)	—
V [Re(CO) <sub>2</sub> {N(NC <sub>6</sub> H <sub>4</sub> p-CH <sub>3</sub> ) <sub>2</sub> }(PPh <sub>3</sub> ) <sub>2</sub> ]	251 (dec)	yellow- orange	85	62.27 (63.00)	4.61 (4.47)	3.79 (4.24)	—
VI [Re(CO) <sub>2</sub> {N(NC <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> }(PPh <sub>3</sub> ) <sub>2</sub> ]·CH <sub>2</sub> Cl <sub>2</sub>	236 (dec)	orange	86	58.12 (58.45)	3.97 (4.04)	3.99 (4.01)	5.52 (6.77)
VII [Re(CO) <sub>2</sub> {N(NC <sub>6</sub> H <sub>4</sub> p-Cl) <sub>2</sub> }(PPh <sub>3</sub> ) <sub>2</sub> ]	277 (dec)	yellow	83	57.37 (58.18)	3.80 (3.71)	3.76 (4.07)	6.79 (6.87)
VIII [Re(CO) <sub>2</sub> {N(NC <sub>6</sub> H <sub>4</sub> p-F) <sub>2</sub> }(PPh <sub>3</sub> ) <sub>2</sub> ]	274 (dec)	yellow	85	59.30 (60.10)	3.79 (3.83)	4.12 (4.20)	—

Complexes (A) form invariably with no detectable traces of carbamoyl derivatives, as suggested by the absence of a band at *ca.* 1700–1600 cm<sup>-1</sup> in the i.r. spectrum, which is present in the carbamoyl complexes obtained by interacting Li(ArN...CH...NAr) for example, with [M(CO)<sub>5</sub>Cl] at r.t. (M = Mn, Re) [20].

It has been pointed out by other authors that carbonyl ligands having relatively high  $\nu(\text{C}\equiv\text{O})$  may be subjected to nucleophilic attack [23]. However, even though the i.r. spectra of [M(CO)<sub>5</sub>Cl], [M(CO)<sub>4</sub>-Cl]<sub>2</sub> or [Re(CO)<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>Cl] show at least a  $\nu(\text{C}\equiv\text{O})$  at a (comparable) relatively high value (*ca.* 2050 cm<sup>-1</sup>, [23, 24]) the carbamoyl derivative is isolated only starting with the first complex and with the formamidino anion [20, 22]. Starting with [Re(CO)<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>Cl] carbamoyl derivatives are not isolated even when operating under those conditions that would likely favour their formation (*i.e.* by adding a THF solution of Li(ArN...X...NAr) to a THF solution of [Re(CO)<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>Cl] at r.t., in the dark [26]). In the related reaction between [M( $\pi$ -C<sub>5</sub>H<sub>5</sub>)(CO)<sub>3</sub>Cl] (M = Mo, W) and K(ArN...CH...NAr),

both formamidino and carbamoyl complexes form in a molar ratio which depends on i) nature of the metal, ii) nature of the ligand, and iii) reaction conditions. As the first point, the observation that relatively more of the carbamoyl complex is formed for M = Mo than M = W, was explained by assuming that when M = W the electron density on the metal is smaller than in the case of M = Mo. As a result, the attack of the nitrogen lone pair on the W metal atom will be more favoured than for Mo.

Alternatively to reaction pathway (a), where the formamidino anion directly attacks a carbonyl group, the formation of the carbamoyl linkage has been proposed also as resulting from the attack of the imino nitrogen upon a carbonyl ligand (reaction pathway (b) [20, 26]). As the second point, no predictions about the influence of Ar on the reaction pathway could be made. Regarding the third point it was observed that slow addition of the potassium formamidino solution to a [MoCp(CO)<sub>3</sub>Cl] solution, so that an excess of the complex is present throughout the reaction, results in the formation of the carbamoyl complex as the main product. Moreover



it was found that increasing the reaction time did not change the molar ratios of the complexes. Thus it was concluded that decarbonylation of the carbonyl complex did not occur [26].

The i.r. spectra of complexes (A) exhibit two  $\nu(\text{C}\equiv\text{O})$  below  $2000\text{ cm}^{-1}$  (see Table II). Slightly higher values of  $\nu(\text{C}\equiv\text{O})$  are observed in the triazenido derivatives. Variation of the *para* substituents in the phenyl ring causes small changes in  $\nu(\text{C}\equiv\text{O})$ . Substitution of  $\text{Cl}^-$  and CO ligands with  $(\text{ArN}\equiv\text{X}\equiv\text{NAr})^-$  causes a marked lowering in the  $\nu(\text{C}\equiv\text{O})$  values (in  $[\text{Re}(\text{CO})_3(\text{PPh}_3)_2\text{Cl}]$   $\nu(\text{C}\equiv\text{O})$  appears at 2045w, 1940s, and 1885s  $\text{cm}^{-1}$  [25]). It is interesting to observe that substitution of  $\text{Cl}^-$  and CO with  $(\text{ArN}\equiv\text{CH}\equiv\text{NAr})^-$  in  $[\text{Re}(\text{CO})_5\text{Cl}]$  (2056, 1987  $\text{cm}^{-1}$ ) [24] leads to particularly high values of  $\nu(\text{C}\equiv\text{O})$  (in  $[\text{Re}(\text{CO})_4(\text{ArN}\equiv\text{CH}\equiv\text{NAr})]$   $\nu(\text{C}\equiv\text{O})$  occurs at ca. 2110, 2010, 1990, and 1950  $\text{cm}^{-1}$ ) [20, 27].

The most significant i.r. bands for the  $(\text{ArN}\equiv\text{X}\equiv\text{NAr})^-$  ligand occur at ca. 1290–1220  $\text{cm}^{-1}$ . The i.r. absorption bands for the 1,3-diaryltriazenido ligand have been classified into two classes. One class shows bands at ca. 1300–1260  $\text{cm}^{-1}$  for the chelating ligand; the other class shows bands also at 1380–1360, 1220, and 1150  $\text{cm}^{-1}$  for the ligand acting as bridging or monodentate [17]. The triazenido complexes here reported do not show any band at 1380–1360  $\text{cm}^{-1}$ , thus the ligand is supposed to act as chelating<sup>§</sup>. It is also likely that the closely related formamidino ligand acts similarly as chelating.

The  $^1\text{H}$  n.m.r. spectra of  $[\text{Re}(\text{CO})_2(\text{PPh}_3)_2(\text{ArN}\equiv\text{CH}\equiv\text{NAr})]$  show the CH proton as a not well resolved multiplet downfield with respect to that proton of  $\text{ArNHCHNAr}$  which appears as a singlet. The aryl proton groups of  $(\text{ArN}\equiv\text{X}\equiv\text{NAr})^-$  in the complex appear as a AA'BB' multiplet centered at a higher field with respect to the same protons of  $\text{ArNHXNAr}$ . An analogous trend was observed in the related complexes of the type  $[\text{M}(\text{CO})_4(\text{ArN}\equiv\text{X}\equiv\text{NAr})]$  [20, 27]. The unique methyl signal (at ca. 7.7 $\tau$ ) suggests that the methyl groups are equivalent (no low temperature  $^1\text{H}$  n.m.r. spectra was recorderd in order to ascertain whether the  $\text{CH}_3$  equivalence is due to the molecular geometry found in the solid<sup>†</sup>, or to a fluxional behaviour of the ligand acting as monodentate in solution [1, 2, 14].

## Experimental

Solvents were purified and dried before use.  $\text{ArNHCHNAr}$  [29],  $\text{ArNHN}_2\text{Ar}$  [30], and *trans*- $[\text{Re}(\text{CO})_3(\text{PPh}_3)_2\text{Cl}]$  [25] were prepared following literature methods. Other materials were reagent grade chemicals.

### I.r.

<sup>†</sup>This has been confirmed by X-ray diffraction studies on  $[\text{Re}(\text{CO})_2(p\text{-CH}_3\text{C}_6\text{H}_4\text{N}_3\text{C}_6\text{H}_4\text{CH}_3\text{-}p)(\text{PPh}_3)_2]$ , in which the carbonyl and the triazenido ligands lie in the equatorial plane of an octahedral geometry [28].

TABLE II. Spectroscopic Data.

Compound	IR ( $\text{cm}^{-1}$ ) Nujol mull		UV absorption maximum		$^1\text{H}$ NMR ( $\text{CDCl}_3$ ) <sup>b</sup>		
	$\nu(\text{C}\equiv\text{O})$	$\nu(\text{ArN}\equiv\text{X}\equiv\text{NAr})^a$	$\lambda(\text{m}\mu)$	$\epsilon_{\text{max}}$	Aryl protons	CH	$\text{CH}_3$
I $[\text{Re}(\text{CO})_2\{\text{CH}(\text{NC}_6\text{H}_4p\text{-CH}_3)_2\}(\text{PPh}_3)_2]$	1893vs 1815vs	1520vs, 1257s	386	14,600	3.52(m) (3.00)	1.56(m) (1.90)	7.70(s) (7.8)
II $[\text{Re}(\text{CO})_2\{\text{CH}(\text{NC}_6\text{H}_5)_2\}(\text{PPh}_3)_2]$	1900vs 1820vs	1520vs, 1268vs 1230m	384	11,000	3.42(m) (2.70)	1.25(m) (1.75)	
III $[\text{Re}(\text{CO})_2\{\text{CH}(\text{NC}_6\text{H}_4p\text{-Cl})_2\}(\text{PPh}_3)_2]$	1910vs 1825vs	1620vs, 1278s 1258s, 1228m	393	16,400	3.50(m) (2.84)	1.50(m) (1.93)	
IV $[\text{Re}(\text{CO})_2\{\text{CH}(\text{NC}_6\text{H}_4p\text{-F})_2\}(\text{PPh}_3)_2]$	1915vs 1828vs	1530vs, 1260s 1218s	378	9,600	3.62(m) (2.95)	1.52(m) (1.98)	
V $[\text{Re}(\text{CO})_2\{\text{N}(\text{NC}_6\text{H}_4p\text{-CH}_3)_2\}(\text{PPh}_3)_2]$	1920vs 1834vs	1278s	445	10,400	3.47(m) (2.77)		7.80(s) (7.68)
VI $[\text{Re}(\text{CO})_2\{\text{N}(\text{NC}_6\text{H}_5)_2\}(\text{PPh}_3)_2]$	1900vs 1830vs	1268s	440	11,000	3.33(m) (2.62)		
VII $[\text{Re}(\text{CO})_2\{\text{N}(\text{NC}_6\text{H}_4p\text{-Cl})_2\}(\text{PPh}_3)_2]$	1925vs 1840vs	1290s 1275s	450	13,400	3.42(m) (2.66)		
VIII $[\text{Re}(\text{CO})_2\{\text{N}(\text{NC}_6\text{H}_4p\text{-F})_2\}(\text{PPh}_3)_2]$	1918vs 1838vs	1295s 1280s	440	8,600	3.50(m) (2.77)		

<sup>a</sup>Only main bands associated with the triazenido- or formamidino-linkages.

<sup>b</sup>In parentheses the corresponding values for the ligand  $\text{ArNHXNAr}$ .

I.r. and  $^1\text{H}$  n.m.r. spectra were recorded on a Perkin Elmer 577 and on W.P.80 MHz Bruker spectrometers, respectively.

*Preparation of  $[\text{Re}(\text{CO})_2(\text{PPh}_3)_2(\text{ArN}=\text{X}=\text{NAr})]$  ( $\text{X} = \text{CH}, \text{N}$ )*

For both classes of complexes we followed the same procedure. In a typical experiment, a solution of *n*-butyllithium in exane (0.24 ml *ca.* 2 M, 0.48 mmol) was added to a dry THF solution of (Ar-NHXNAr) (Ar = *p*- $\text{CH}_3\text{C}_6\text{H}_4$ ,  $\text{C}_6\text{H}_5$ , *p*- $\text{ClC}_6\text{H}_4$ , *p*- $\text{FC}_6\text{H}_4$ ) (40 ml, 0.48 mmol) at r.t. under nitrogen atmosphere. Solid *mer*- $[\text{Re}(\text{CO})_3(\text{PPh}_3)_2\text{Cl}]$  (0.2 g, 0.24 mmol) was added to the solution in which it dissolved in a few minutes while heating to b.p., yielding a light yellow solution. The solution was refluxed for three hours under nitrogen. No colour change was observed during this period. The mixture was then concentrated to 1/3 of its volume and filtered. A yellow powder was obtained by adding EtOH to the solution. The solid was washed with  $\text{H}_2\text{O}$ , EtOH, dried, and crystallized from  $\text{CH}_2\text{Cl}_2/\text{EtOH}$ .

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#### References

- 1 K. R. Laing, S. D. Robinson and M. F. Uttley, *J. Chem. Soc. Dalton Trans.*, 1205 (1974).
- 2 L. Toniolo, A. Immirzi, U. Croatto and G. Bombieri, *Inorg. Chim. Acta*, 19, 209 (1976).
- 3 L. D. Brown and J. A. Ibers, *J. Amer. Chem. Soc.*, 98, 1597 (1976).
- 4 E. Pfeiffer, J. Kuyper and K. Vrieze, *J. Organometal. Chem.*, 105, 371 (1976) and reference therein.
- 5 M. Corbett and B. F. Hoskins, *J. Amer. Chem. Soc.*, 89, 1530 (1967).
- 6 P. I. van Vliet, J. Kuyper and K. Vrieze, *J. Organometal. Chem.*, 122, 99 (1976).
- 7 M. Corbett and B. F. Hoskins, *J. Chem. Soc. Chem. Comm.*, 1602 (1968).
- 8 J. E. O'Connor, G. A. Janusonis and E. R. Carey, *J. Chem. Soc. Chem. Comm.*, 445 (1968).
- 9 I. D. Brown and J. A. Dunitz, *Acta Cryst.*, 14, 480 (1961).
- 10 P. Hendriks, J. Kuyper and K. Vrieze, *J. Organometal. Chem.*, 120, 285 (1976).
- 11 S. Candeloro de Sanctis, N. V. Pavel and L. Toniolo, *J. Organometal. Chem.*, 108, 409 (1976).
- 12 J. Kuyper, P. I. van Vliet and K. Vrieze, *J. Organometal. Chem.*, 105, 379 (1976) and references therein.
- 13 W. Bradley and I. Wright, *J. Chem. Soc.*, 640 (1956).
- 14 T. Boschi, U. Belluco, L. Toniolo, R. Faver and R. Roulet, *Inorg. Chim. Acta*, 23, 37 (1979).
- 15 P. I. van Vliet, M. Kokkes, G. van Koten and K. Vrieze, *J. Organometal. Chem.*, 187, 413 (1980).
- 16 P. I. van Vliet, M. Kokkes, G. van Koten and K. Vrieze, *J. Organometal. Chem.*, 188, 301 (1980).
- 17 E. Pfeiffer, A. Oskam and K. Vrieze, *Trans. Met. Chem.*, 2, 240 (1977).
- 18 L. Toniolo and G. Cavinato, *Inorg. Chim. Acta Letters*, 35, L301 (1979).
- 19 L. Toniolo, *Inorg. Chim. Acta*, 35, L367 (1979).
- 20 E. W. Abel and S. J. Skittrai, *J. Organometal. Chem.*, 185, 391 (1980).
- 21 R. B. King and K. C. Nainan, *Inorg. Chem.*, 14, 271 (1975).
- 22 E. W. Abel and I. D. H. Towle, *J. Organometal. Chem.*, 155, 299 (1978).
- 23 R. J. Angelici, *Acc. Chem. Res.*, 5, 335 (1972).
- 24 E. W. Abel, G. B. Hargreaves and G. Wilkinson, *J. Chem. Soc.*, 3149 (1958).
- 25 J. Chatt, J. R. Dilworth, H. P. Gunz and G. J. Leigh, *J. Organometal. Chem.*, 84, 245 (1974).
- 26 W. H. De Roode and K. Vrieze, *J. Organometal. Chem.*, 153, 345 (1978).
- 27 E. W. Abel and I. D. H. Towle, *J. Organometal. Chem.*, 155, 299 (1978).
- 28 A. Casellato, R. Graziani, R. Rossi, L. Magon and L. Toniolo, *Inorg. Chim. Acta*, to be published.
- 29 Beilstein, 12, 919; I, 419.
- 30 *Organic Syntheses*, Collect. Vol. II, Wiley, New York, p. 163 (1943).