given U(VI) concentration in chloride than in perchlorate solutions.

On the basis of recent acidity measurements by other workers in this Laboratory,[39] it was concluded that the (3,4) species also is not important in nitrate solutions. From this point of view, nitrate media seem more similar to perchlorate than chloride media, a conclusion which is consistent with the phase diagrams.[38] The degrees of polymerization are, of course, (Fig. 3) not very sensitive to these differences in hydrolysis in the various media, since only different trimers are involved.

A report is in preparation containing the acidity data, information on the least squares fitting program, and other details relative to this article. The report, ORNL-3278, will be available from the Office of Technical Services, Department of Commerce, Washington 25, D.C.

Acknowledgment.—We wish to express indebtedness to Neva Harrison for technical assistance, and to Professor George Scatchard for helpful discussions.

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[39] C. F. Baes, Jr., and N. J. Meyer, Paper No. 105, Inorganic Div., 140th National Meeting of the American Chemical Society, Chicago, Ill., 1961.

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Chemistry of the Metal Carbonyls. XVI. Synthesis of Dicarbonyldinitrosyliron(0)[1,2]

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Nitrosyl chloride and iron pentacarbonyl react to give dicarbonyldinitrosyliron(0) in good yields. Some new phosphine and arsine complexes derived from dicarbonyldinitrosyliron(0) are reported, and their infrared spectra are discussed and compared with those of related complexes.

As part of a study of reactions between metal carbonyls and compounds having *pseudo*-halogen properties, we investigated the action of nitrosyl chloride on iron pentacarbonyl. We found that this reaction gives dicarbonyldinitrosyliron(0) in good yield. Since both iron pentacarbonyl and nitrosyl chloride are obtainable readily this represents a much easier route to the compound $Fe(CO)_2(NO)_2$ than the previously known syntheses from triiron dodecacarbonyl or iron enneacarbonyl and nitric oxide,[3a] or *via* the carbonyl hydride and sodium nitrite.[3b] With relatively large quantities of dicarbonyldinitrosyliron(0) available, we were led to investigate some of its reactions with ligands having a Group V element as the donor atom, and with unsaturated organic compounds.

A few complexes derived from dicarbonyldinitrosyliron(0) and Group V ligands have been reported previously,[4] including the compounds $[(C_6H_5)_3P]_2Fe(NO)_2$, $(C_6H_5)_3AsFe(CO)(NO)_2$, and $(C_6H_5)_3SbFe(CO)(NO)_2$. We describe the related compounds $(C_6H_5)_3PFe(CO)(NO)_2$ and $[(C_6H_5)_3As]_2Fe(NO)_2$, substances not obtained by the previous investigators, as well as the chelate complex $[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]Fe(NO)_2$ (Table I).

Several attempts were made to replace the carbonyl groups in dicarbonyldinitrosyliron(0) with various unsaturated organic ligands in the hope of obtaining diene–iron dinitrosyl compounds, analogous to the many known diene–iron tricarbonyl complexes. Reactions with bicycloheptadiene, diphenylacetylene, cycloöctatetraene, and cycloheptatriene were investigated. All gave evidence of reaction, but in every case the solutions of product were found to be extremely unstable and air-sensitive, and no iron containing products were isolated.

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[1] Previous article in this series, R. B. King, S. L. Stafford, P. M. Treichel, and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 3604 (1961).

[2] This work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research.

[3] (a) W. Hieber and J. S. Anderson, *Z. anorg. u. allgem. Chem.*, **208**, 238 (1932); **211**, 132 (1933); (b) F. Seel, *ibid.*, **269**, 40 (1952).

[4] M. Malatesta and A. Araneo, *J. Chem. Soc.*, 3803 (1957).

TABLE I

SOME NEW IRON NITROSYL COMPLEXES[a]

Compound	M.p., °C.	Carbon, %		Hydrogen, %		Nitrogen, %	
		Calcd.	Found	Calcd.	Found	Calcd.	Found
$(C_6H_5)_3PFe(CO)(NO)_2$	138–140 dec.	56.2	55.6	3.69	3.73	6.90	6.71
$[(C_6H_5)_3As]_2Fe(NO)_2$[b]	154–156 dec.	59.3	59.2	4.12	4.31	3.85	3.82
$[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]Fe(NO)_2$	147–150 dec.	60.7	59.8	4.70	4.73	5.44	5.30

[a] Microanalyses performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., and by Dr. A. Bernhardt, Max Planck Institut für Kohlenforschung, Mülheim, Germany. [b] Fe, calcd. 7.7, found 8.0%; As, calcd. 20.6, found 20.3%.

Experimental

All reagents were commercial samples, with the exception of 1,2-bis(diphenylphosphoryl)ethane, which was prepared by the method of Chatt and Hart.[5]

Preparation of Dicarbonyldinitrosyliron(0). Method A.—Iron pentacarbonyl (24.5 g., 125 mmoles) and nitrosyl chloride (12.4 g., 190 mmoles) were distilled into an evacuated 150-ml. stainless steel bomb. The bomb was sealed and allowed to stand at room temperature (~25°) for 24 hr. The bomb then was cooled to $-196°$ and carbon monoxide was pumped off. Warming to room temperature caused 7.6 g. of red liquid to distil under high vacuum from the bomb into a trap cooled to $-78°$. Vapor phase chromatography, using a silicone on firebrick column at 40° and a 250 cc./min. flow of helium as carrier, showed this to be a mixture of 65% dicarbonyldinitrosyliron(0) (elution time 6.5 min.) and 35% iron pentacarbonyl (elution time 4 min.), representing a 50% yield of the iron nitrosyl based on iron pentacarbonyl consumed.[6] Other preparations using larger proportions of nitrosyl chloride gave pure dicarbonyldinitrosyliron(0), identified by its infrared spectrum[7] and gas density (mol. wt. calcd., 172; found, 175), but in lower yields. As an extreme example of the detrimental effect of excess of nitrosyl chloride on yield, a reaction between 57 mmoles of nitrosyl chloride and 21 mmoles of iron pentacarbonyl gave only a mixture of carbon monoxide and nitrogen oxides as volatile products, no dicarbonyldinitrosyliron(0) being isolated.

Method B.—A three-necked flask fitted with a Dry Ice condenser, stirrer, and gas inlet was flushed with prepurified nitrogen, and 19 ml. (141 mmoles) of iron pentacarbonyl and 25 ml. of pentane were introduced. Nitrosyl chloride (10.2 g., 156 mmoles) was passed into the flask over a period of 1.5 hr. The reaction is not exothermic. After standing overnight the volatile contents were pumped from the flask at reduced pressure into a $-78°$ trap. In order to remove the pentane the material was distilled into a vacuum line through U-traps maintained at -63, -78, and $-196°$. Pentane was collected in the $-196°$ trap, and the iron nitrosyl containing some iron pentacarbonyl was found in the $-63°$ trap. It was refractionated, material passing a $-45°$ trap being discarded. In this manner 8.0 g. of a dicarbonyldinitrosyliron(0)–iron pentacarbonyl mixture, shown by vapor phase chromatography to contain 70% of the nitrosyl, was obtained.[6]

Preparation of Complexes. $(C_6H_5)_3PFe(CO)(NO)_2$ and $[(C_6H_5)_3P]_2Fe(NO)_2$.—Triphenylphosphine (9.2 g., 35 mmoles) and dicarbonyldinitrosyliron(0) (3.8 g., 22 mmoles) were sealed together in an evacuated reaction bulb and heated for 16 hr. at 85°. The resulting dark solid was chromatographed on alumina. A 1:4 dichloromethane–pentane mixture rapidly eluted an orange band, which left 3.5 g. (96% of expected yield) of deep red solid after removal of solvent. Recrystallization from dichloromethane–pentane at $-78°$ gave analytically pure $(C_6H_5)_3PFe(CO)(NO)_2$[8] (Table I).

Continued elution using 1:1 dichloromethane–pentane brought down an olive-green band which gave a red-black solution. Solvent was removed and black crystals (8 g., 95% of expected yield) of $[(C_6H_5)_3P]_2Fe(NO)_2$ were obtained, m.p. 205° after recrystallization (lit.,[4] 194°). *Anal.* Calcd. for $C_{36}H_{30}O_2N_2P_2Fe$: C, 67.5; H, 4.7; N, 4.4. Found: C, 67.1; H, 4.7; N, 4.5.

$(C_6H_5)_3AsFe(CO)(NO)_2$ and $[(C_6H_5)_3As]_2Fe(NO)_2$.—Following an entirely analogous procedure, the complexes $(C_6H_5)_3AsFe(CO)(NO)_2$ (m.p. 110–115° (decomp.); lit.,[4] 100–110° (decomp.)) and $[(C_6H_5)_3As]_2Fe(NO)_2$ (Table I) were obtained.

$(C_6H_5)_3SbFe(CO)(NO)_2$.—A reaction between triphenylstibine and dicarbonyldinitrosyliron(0) was carried out in a manner similar to that described above for triphenylphosphine. However, chromatography in the usual way gave only one product, no olive band being observed. Infrared spectroscopy identified the compound isolated as $(C_6H_5)_3SbFe(CO)(NO)_2$, although the complex was extremely unstable and difficult to purify, and a melting point could not be obtained.

$[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]Fe(NO)_2$.—1,2-Bis(diphenylphosphoryl)ethane (4.5 g., 11 mmoles) was added to a solution of dicarbonyldinitrosyliron(0) (1.5 g., 9 mmoles) in 40 ml. of cyclohexane. The mixture was warmed gently overnight, chromatographed on alumina, and finally eluted with dichloromethane–pentane mixtures. In this manner the complex $[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]Fe(NO)_2$ (Table I) was recovered (2.0 g., 45% yield). An analytical sample was recrystallized from cyclohexane as red-brown platelike crystals.

Discussion

The infrared carbonyl and nitrosyl stretching bands of the new nitrosyl complexes as well as those of some previously characterized[4] compounds were recorded, and are listed in Table II.

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(5) J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1378 (1960).

(6) As has been noted previously,[3] dicarbonyldinitrosyliron(0) is somewhat unstable above 0°. Therefore, during chromatography some decomposition of the nitrosyl was observed. Hence the yield and purity of the compound must have been higher than the chromatographic results suggest.

(7) C. G. Barraclough and J. Lewis, *J. Chem. Soc.*, 4842 (1960).

(8) We are indebted to a referee for drawing our attention to the article by W. Hieber, W. Beck, and H. Tengler, *Z. Naturforsch.*, **15b**, 411 (1960), where this compound receives very brief mention.

TABLE II

CARBONYL AND NITROSYL INFRARED STRETCHING FREQUENCIES[a]

Compound	Carbonyl frequency, cm.$^{-1}$	Nitrosyl frequency, cm.$^{-1}$
$Fe(CO)_2(NO)_2$[b]	2087, 2034	1810, 1756
$(C_6H_5)_3PFe(CO)(NO)_2$	2009 (s)	1764 (s), 1722 (vs)
$(C_6H_5)_3AsFe(CO)(NO)_2$	2010 (s)	1767 (s), 1726 (vs)
$(C_6H_5)_3SbFe(CO)(NO)_2$	2010 (s)	1771 (s), 1728 (vs)
$[(C_6H_5)_3P]_2Fe(NO)_2$	. . .	1724 (s), 1678 (vs)
$[(C_6H_5)_3As]_2Fe(NO)_2$	. . .	1732 (s), 1690 (vs)
$[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]Fe(NO)_2$	. . .	1726 (s), 1679 (vs)

[a] The spectra were recorded with a Perkin–Elmer Model 21 spectrophotometer having a calcium fluoride prism. The frequencies recorded refer to tetrachloroethylene solutions. Within experimental error the band positions were not changed in cyclohexane solution. [b] From ref. 7 (cyclohexane solution).

The band positions may be interpreted readily in terms of current views on the nature of the bonding in compounds of this type.[9] The metal–carbon and metal–nitrogen linkages are believed to involve both σ- and π-bonds, the latter serving to disperse negative charge from the metal, thereby increasing the stability of the compounds. The ligands $(C_6H_5)_3M$ (M = P, As, Sb) are considered to be poorer electron acceptors than is the carbonyl group.[10] Therefore, when one of the carbonyl groups of dicarbonyldinitrosyliron(0) is replaced by a $(C_6H_5)_3M$ group, we should anticipate an increase in metal–carbon π-bonding with a consequential lowering of the C–O stretching frequency of the remaining metal carbonyl. The results presented in Table II are in agreement with this idea, and it is interesting to note that the carbonyl frequency apparently is independent of the nature of M in $(C_6H_5)_3M$. The nitrosyl stretching frequencies (Table II) also fall as carbonyl groups in dicarbonyldinitrosyliron(0) are substituted by ligands of the Group V elements. This is as expected if the resonance form M=N=O makes a greater contribution as carbonyl groups are replaced, increased back donation of electrons from the metal to the nitrosyl group being a mechanism by which the metal may compensate for the relatively poor acceptor properties of the $(C_6H_5)_3M$ ligands. The negative charge on the metal must be dispersed by the nitrosyl, and any remaining carbonyl groups, if the complex is to have reasonable stability.

In many metal nitrosyl compounds, nitric oxide molecules may be considered to donate an electron to the metal, and then to behave like the isoelectronic carbonyl group. This implies relatively greater electron transfer to the metal in nitrosyls than in carbonyls. Perhaps this accounts for the lesser stability of metal nitrosyls in general, and in particular for our inability to isolate stable diene–iron dinitrosyls in cases in which a very stable diene–iron tricarbonyl is known, for dienes are particularly poor electron acceptors. We cannot, however, dismiss the possibility of a contribution to instability resulting from the different hybridization about the central iron atom.

Acknowledgment.—We are indebted to Miss E. Pitcher for recording the infrared spectra.

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(9) (a) J. W. Cable and R. K. Sheline, *Chem. Revs.*, **56**, 1 (1956); (b) J. Chatt, P. L. Pauson, and L. M. Venanzi, Chapter 10, "Organometallic Chemistry" (Ed. H. Zeiss), Am. Chem. Soc., Monograph 147, Reinhold Publ. Corp., New York, N. Y., 1960; (c) R. S. Nyholm, *Proc. Chem. Soc.*, 273 (1961).

(10) (a) J. Chatt, L. A. Duncanson, and L. M. Venanzi, *J. Chem. Soc.*, 4456 (1955); (b) L. E. Orgel, *J. Inorg. & Nuclear Chem.*, **2**, 137 (1956); (c) L. S. Meriwether and M. L. Fiene, *J. Am. Chem. Soc.*, **81**, 4200 (1959).