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Appendix

The calculations were of the extended-Hückel type using parameters (see Table III) taken from previous work.[2a] A "weighted H_{ij}" formula was used in all calculations.[20] Distances not previously indicated are S–H = 1.33 Å, Co–S = 2.26 Å, P–H = 1.44 Å, Co–P = 2.16 Å, Co–N = 1.83 Å, and N–O = 1.19 Å.

Registry No. $Cp_2Co_2(CO)_2^{2-}$, 68813-14-9; $Cp_2Co_2(CO)_2^{-}$, 58543-12-7; $Cp_2Co_2(CO)_2$, 58496-39-2; $Cp_2Co_2(NO)_2$, 51862-20-5; $Cp_2Co_2(NO)_2^{+}$, 68875-56-9; $Cp_2Co_2(NO)_2^{2+}$, 68813-15-0; $Co_2(CO)_8$, 10210-68-1; $Co_2(CO)_6(PH_2)_2$, 68813-16-1.

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Metal Derivatives of Azoles. 3.[1a] The Pyrazolato Anion (and Homologues) as a Mono- or Bidentate Ligand: Preparation and Reactivity of Tri-, Bi-, and Mononuclear Gold(I) Derivatives[1b]

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Stable gold(I) derivatives of several azoles, $[Au(az)]_n$, are obtained by various routes (azH = pyrazole or various 1-unsubstituted pyrazoles, benzo-1,2,3-triazole, or 1,2,4-triazole). In these compounds the az^- group acts as an exobidentate *N,N′* ligand; in several cases $n = 3$, and a trinuclear, enneaatomic ring structure is suggested. On the other hand, in the monomeric compounds $Ph_3PAu(az)$ where azH is benzotriazole or 3,5-dimethyl-4-nitropyrazole (pz′H) the azolato anion is monodentate. The compound $Ph_3PAu(pz')$ reacts with $[(CO)_2RhCl]_2$ affording $(CO)_2Rh(\mu\text{-}pz')_2Rh(CO)_2$ and with fluoboric acid or $AgBF_4$ yielding $[Ph_3PAu(\mu\text{-}pz')AuPPh_3]^+BF_4^-$, where only one exobidentate pyrazolato-*N,N′* bridges two gold atoms. The trimeric gold(I) pyrazolates, $Au_3(pz)_3$, react with iodine to give $Au_3(pz)_3I_2$, probably mixed-valence compounds, while with *sym*-trinitrobenzene an unstable 1:1 charge-transfer adduct is obtained and with iodine chloride the coordinated ligand is iodinated in the 4-position affording tris(3,5-dimethyl-4-iodopyrazolato-*N,N′*)trigold(I).

Introduction

Pyrazoles[3] are weak bases and fair nitrogen ligands thanks to the tertiary nitrogen atom. 1-Unsubstituted pyrazoles (pzH)[4] are also very weak acids. Indeed, they react with metallic potassium affording K^+pz^-,[5] with Grignard reagents, PhMgX, yielding pzMgX,[6] or with certain hydrides, such as alkali metal borohydrides, to give hydrogen and the corresponding poly(1-pyrazolyl)borate,[7,8] $M^+[(pz)_nBH_{4-n}]^-$ ($n = 2$, 3, or 4 according to the conditions employed[9]), where the pyrazolato ligands are monodentate. Other species where the

pz^- ligand is monodentate are rare and include the related $[R_{4-n}B(pz)_n]^-$[7,8] or $[Me_2Ga(pz)_2]^-$[10] anions or the recently obtained neutral species $L''Pt(pz)_2$ where L'' is $Ph_2ECH_2CH_2EPh_2$ (E is either P[11] or As[12a]) or α,α′-bipyridyl.[12b]

In turn all these species may be anionic or neutral, metal-containing, polydentate ligands so that, upon reaction with acceptors, the resulting adducts contain two (or more) coordination centers connected by exobidentate pyrazolato-*N,N′* ligands, e.g., $[(\text{chelating ligand})Pt(\mu\text{-pz-}N,N')_2]Ni^{2+}$,[11,12b] $[Me_2Ga(\mu\text{-pz-}N,N')_2]Ni^{2+}$,[10] $[R_2B(\mu\text{-pz-}N,N')_2]_3Co$,[7] or $H_2B(\mu\text{-pz-}N,N')_2Rh(CO)_2$.[13]

Apart from the few examples, listed above, of monodentate behavior, the pyrazolato groups are, generally, such good exobidendate donors that when a suitable acceptor is not immediately available, a coordination polymer is obtained as in the case of $[Ag(\mu\text{-pz-}N,N')]_n$[14,15] or of certain metal(II) pyrazolates, $[M(\mu\text{-pz-}N,N')_2]$, where M is Fe, Co, Ni, Cu, Zn, Cd, etc.[7,16]

Instead of a coordination polymer a discrete molecule may be obtained: dimers such as $[(CO)_2Rh(\mu\text{-pz-}N,N')]_2$[17] or $[(\mu\text{-}C_5H_5)Ni(3,5\text{-}Me_2\text{-pz-}N,N')]_2$,[18] trimers of the type described in a preliminary communication[19] and here below or such as $[Ni(\mu\text{-Pz-}N,N')_2]_3$,[18] or even a tetramer, $[(4\text{-}i\text{-}C_3F_7\text{-pz})Ag]_4$,[20] may result if suitable end-capping groups are present or if the conditions for ring closure are satisfied.

In this paper the preparation and some aspects of the general reactivity are reported of gold compounds which take advantage of exobidentate pyrazolato-*N,N′* ligands to give trinuclear enneaatomic rings, I–VIII, or binuclear complexes (XVII or XVIII). In addition, examples of monodentate azolato derivatives $Ph_3PAu(az)$ (XI or XII) are reported.

Results and Discussion

Gold(I) Derivatives. The preparation of the gold(I) azolates I–XII (Chart I) was carried out according to one or more of the following reactions, where azH means a 1-unsubstituted azole, e.g., a pyrazole pzH:

$$Me_2SAuCl + azH + KOH = (1/n)[Au(az)]_n + KCl + H_2O + Me_2S \quad (1)$$

$$[(3,5\text{-}Me_2\text{-pz})Au]_3 + 3ICl = [(3,5\text{-}Me_2\text{-}4\text{-I-pz})Au]_3 + 3HCl \quad (2)$$

$$Ph_3PAuCl + azH + KOH = Ph_3PAu(az) + KCl + H_2O \quad (3)$$

$$Ph_3PAu(az) \rightleftarrows Ph_3P + (1/n)[(az)Au]_n \quad (4)$$

All the pyrazolates I–VIII (except V), the 1,2,4-triazolate X, and the benzo-1,2,3-triazolate IX could be obtained according to reaction 1 as colorless compounds, generally sparingly soluble or insoluble in organic solvents. All these compounds are thermally stable at least up to 140 °C; but their stability to heat and light is dramatically lowered by impurities, especially from those which may be present in aged samples of Me_2SAuCl. The attempted preparations of 3,5-dimethyl-4-iodopyrazolatogold(I), V, as well as of the 4-Cl and 4-Br homologues, were unsuccessful according to reaction 1. Indeed, with a reaction time of a few minutes the infrared spectrum of the unstable crude product revealed unreacted Me_2SAuCl, which could not be removed easily, while longer reaction times afforded a decomposed product, as evidenced by the violet color due to finely divided metallic gold. However, treatment of the 3,5-dimethylpyrazolatogold(I), II, with iodine chloride afforded neatly the desired 4-iodo derivative, V, stable and insoluble, according to the reaction of the coordinated ligand (2).

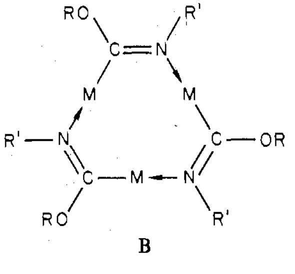
Reaction 3 was carried out with various pyrazoles and with benzo-1,2,3-triazole. In the case of $3,5\text{-}Me_2\text{-}4\text{-}NO_2\text{-pzH}$ (pz′H) it afforded $Ph_3PAu(pz')$, XI, soluble in organic solvents. Remarkably, the related compound without Ph_3P, i.e., $[(pz')Au]_n$, is also stable and could be prepared according to reaction 1.

Other triphenylphosphine adducts could be obtained according to the reaction 3, but they are not as stable as the nitropyrazolate XI. This could be treated with boiling hexane in a Soxhlet extractor for 10 days without removing any Ph_3P according to equilibrium 4. Indeed, both the residue and the extract were found to be the same compound, $Ph_3PAu(pz')$ (XI). Similarly, the neutral ligand could not be removed in the case where az^- was the benzotriazolato anion XII. On the contrary, continuous extraction with boiling hexane succeeded in removing triphenylphosphine from $Ph_3PAu(3,5\text{-}Me_2\text{-pz})$, or from $Ph_3P(3,5\text{-}Me_2\text{-}4\text{-I-pz})Au$, affording the corresponding $[Au(pz)]_n$ as an insoluble residue according to the equilibrium 4, which is the most convenient preparation of compound II.

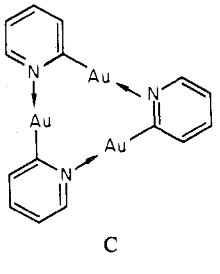
Equilibrium 4 can be shifted from right to left. Actually, while compound II was insoluble in benzene, it went into solution upon addition of Ph_3P, and a solid analyzing as $Ph_3PAu(3,5\text{-}Me_2\text{-pz})$ could be obtained by addition of petroleum ether to the solution, but the crude compound could not be crystallized without loss of triphenylphosphine. The continuous extraction, this time with boiling toluene, was also employed in order to obtain a pure sample of 3,5-dimethyl-4-(*p*-tolylazo)pyrazolatogold(I), VII.

The solubility of the gold pyrazolates can be increased by putting suitable substituents on the ring: consequently compounds III, IV, and VIII are soluble in aromatic and chlorinated solvents, while I and II are soluble (with partial decomposition) only in boiling pyridine. Solubility is not negligible in those compounds which contain triphenylphosphine.

Poor solubility has hindered the determination of the molecular weight in many of the compounds reported. However, osmometry and/or mass spectrometry[21] (Table I)[44] showed that in many cases the value of *n* in eq 1 or 4 is 3. Therefore, although X-ray data are not available, a cyclic structure such as A is suggested. Not only such a structure is compatible with the usual linear sp hybridization of gold(I), with the usual trigonal, sp^2-hybridized nitrogen atoms of the pyrazole, and with the geometrical requirements of a nine-membered, planar ring, but it also fits into a series of trimetallic and probably planar rings where the metal atoms are joined by two sp^2-hybridized atoms. These may be either two nitrogens as in the pyrazolates (A) or one carbon plus one nitrogen as in the $[MC(OR){=}NR']_3$ compounds (B, where M = Au[22,23] or Ag[24]) or in (α-pyridyl)gold(I) (C),[25] or, perhaps, even in (1-methylbenzimidazol-2-yl)gold(I), for which the highest peak found[26] in the mass spectrum does correspond to the trimer.



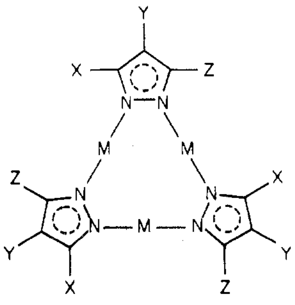
B



C

As a general characteristic, all these compounds (if pure) are stable to air, moisture, and heat. These rather big molecules are sparingly soluble in organic solvents unless a suitable number of alkyl radicals are attached to the ring. Besides gold(I), the metals involved in the enneaatomic ring formation may include silver(I)[24] (B, where M = Ag) or copper(I)[27] (A, where M = Cu and X = Y = Z = H), so that

Chart I



A

	compd								
	I	II	III	IV	V	VI	VII	VIII	...
M	Au	Au	Au	Au	Au	Au	Au	Au	Cu
X	H	Me	Me	Me	Me	Me	Me	Me	H
Y	H	H	H	Et	I	NO_2	$N_2C_6H_4Me$	$(CH_2)_2CH_2$	H
Z	H	Me	Ph	Me	Me	Me	Me		H
prepd according to reacn	1	1 3 + 4 7b	1	1	2 3 + 4	1	1 3 + 4	1	ref 27

even on the scattered and as yet unsystematic evidence available it must be acknowledged that this type of trimetallic and, possibly, planar arrangement is not uncommon in this part of the periodic table.

The stability of such a ring is evidenced in our case not only by its resistence to attacks by acids (see below) and by its ability to undergo a reaction on a coordinated ligand, such as (2), but also by the existence of two isomers in the case of the (3-methyl-5-phenylpyrazolato)gold(I), III, where the anion no longer has the C_2 symmetry axis which is typical of pyrazolato and of 3,5-dialkylpyrazolato anions. An attempt to obtain a more soluble derivative on which the isolation of both the isomers could be tried led to the use of 3-methyl-4,5-trimethylenepyrazole as azH in the reaction 1. Unfortunately, according to the NMR spectrum only the symmetric isomer was present in the reaction product, VIII, probably because the formation of the other isomer is hampered by the steric requirements of the trimethylene chain.

Instead of a trimeric structure of the type A, a polymeric formula like $[(\mu\text{-azolato-}N,N')\text{Au}]_n$ cannot be excluded for those gold(I) derivatives for which insufficient solubility has not allowed the determination of the molecular weight. However, if a compound (e.g., VII) is sparingly soluble but can be extracted by a solvent, a highly polymeric structure is unlikely.

Oligo- or polymerization of the Au(pz) moiety through the other donor nitrogen atom can be avoided if the donor ability of nitrogen is reduced by suitable ring substitution (nitro or benzo group) in the presence of a good ligand on the second coordination site of the gold(I). For example, the monomeric $Ph_3PAu(az)$ compounds are thus obtained where az$^-$ is 3,5-Me_2-4-NO_2-pz$^-$ (XI) or benzo-1,2,3-triazolato (XII). In this respect the behavior of these azolato ligands is quite similar to that of the C(OR)═NR′ anion which is known to give both stable trimers, $[AuC(OR){=}NR']_3$,[22,23] and stable monomers, e.g., $Ph_3PAuC(OMe){=}NC_6H_4$-*p*-Me.[28] The 3,5-Me_2-4-NO_2-pz$^-$ group is fluxional in XI, as is the unsubstituted pyrazolato ion in other compounds, e.g., *N*-(tributylstannyl)pyrazole,[29] but not in other derivatives such as $(Ph_2PCH_2)_2Pt(Pz)_2$ and its homologues:[11,12] indeed, in the NMR spectra of XI only one methyl signal was observed down to −50 °C in $CDCl_3$ or to −70 °C in $(CD_3)_2CO$.

Reactivity of the Gold(I) Derivatives. The trimers are very stable toward alkali, in the presence of which they are formed, and toward acids; besides reaction 2 neither concentrated hydrochloric acid nor hydrogen chloride attacks $[(3,5\text{-}Me_2\text{-}pz)Au]_3$, II. This compound is also unaffected by ethyl iodide, even after 18 h.

Since the related gold(I) compound $Ph_3PAuC(OMe){=}N(p\text{-tolyl})$ is known[30] to react with fluoboric acid, with silver fluoborate, or with $[(CO)_2RhCl]_2$ yielding $[Ph_3PAuC(OMe){=}NHAr]^+BF_4^-$, $[\{Ph_3PAuC(OMe){=}NAr\}_2Ag]^+BF_4^-$, or *cis*-$(CO)_2[Ph_3PAuC(OMe){=}NAr]ClRh$, respectively, these reagents were reacted with $Ph_3PAu(pz')$, XI, but the results obtained were quite different. Indeed, reaction with fluoboric acid afforded a binuclear gold(I) complex, XVII, according to reaction 5a. This is the first compound where two metallic nuclei are bridged only by one pyrazolato-*N,N′* anion. The compound XVII seems to be easily formed, also being the product of the reaction of XI with silver fluoborate (5b). The reaction with dimeric rhodium dicarbonyl chloride led to a binuclear rhodium(I) compound having two μ-pyrazolato-*N,N′* bridging ligands, even in the presence of a methyl group in each position adjacent to the nitrogens (eq 6). A simpler homologue of the compound XVIII having unsubstituted pyrazolato groups in the place of pz′ was obtained by the reaction of $[(CO)_2RhCl]_2$ with pyrazole and triethylamine.[17]

$$2Ph_3PAu(pz') + 2HBF_4 = [pz'H_2]^+BF_4^- + [Ph_3PAu(\mu\text{-}pz')AuPPh_3]^+BF_4^- \quad (5a)$$

$$2Ph_3PAu(pz') + AgBF_4 = (1/n)[Ag(pz')]_n + [Ph_3PAu(\mu\text{-}pz')AuPPh_3]^+BF_4^- \quad (5b)$$

$$\underset{\text{XI}}{2Ph_3PAu(pz')} + [(CO)_2RhCl]_2 = 2Ph_3PAuCl + \underset{\text{XVIII}}{[CO)_2Rh(\mu\text{-}pz')]_2} \quad (6)$$

Reactions with Iodine and with Trinitrobenzene. The reaction of gold(I) pyrazolates with iodine was carried out readily in chloroform. At room temperature or upon heating or even in the presence of excess iodine only 1:1 adducts were isolated according to the reaction

$$\underset{\text{II, III, IV, VIII}}{Au_3(pz)_3} + I_2 \underset{(7b)}{\overset{(7a)}{\rightleftarrows}} \underset{\text{XIII, XV, XIV, XVI, respectively}}{Au_3(pz)_3I_2} \quad (7)$$

Here pzH includes 3,5-Me_2-, 3,5-Me_2-4-Et-, 3-Me-5-Ph-, and

Table III. Proton NMR Spectra[a]

compd	methyl group(s)	aromatic[b]	others
III	8.05 s, 8.01 s, 7.99 s	2.5–1.8	4-CH: 3.75 s, 3.70 s, 3.65 s
IV	7.92 s, 8.95 t ($J = 7$ Hz)		CH_2: 7.79 q ($J = 7$ Hz)
VIII[c]	7.81 s, br		$(CH_2)_3$: 7.50 br
XI	7.37 s[d]	2.5 s	
XII		1.90–3.10	
XIII[e]	7.75 s, 7.71 s, 7.45 s		4-CH: 3.86 s, br
XIV	7.80 s, 7.74 s, 7.57 s 8.92[f] ($J = 7$ Hz)		CH_2: 7.64 q, br
XV	7–8 many singlets	1.8–3.17	4-CH: 3.32–3.68
XVI	7.8 s, br		$(CH_2)_3$: 6.8–8.0 br, m
XVII	7.28 s	2.2–3.0	
XVIII	7.35	2.60 s[g]	

[a] $CDCl_3$ solution in all cases except III (C_6D_6); at 60 MHz, ca. 40 °C, τ units; s = singlet, t = triplet, q = quartet, m = multiplet. Integration supports the assignments given. [b] Always multiplet unless stated otherwise. [c] Spectrum unaltered down to −50 °C. [d] Signal unaltered down to −40 °C, at −55 °C some broadening; in acetone-d_6 the signal is unaltered down to −70 °C. [e] The same spectrum was obtained after allowing the sample to stand for more than 2 h. [f] Two nearly overlapping triplets, ca. 1:2. [g] The analysis suggests independently that 0.33 benzene is clathrated, which is not removed by pumping to constant weight at room temperature and ca. 0.1 mmHg.

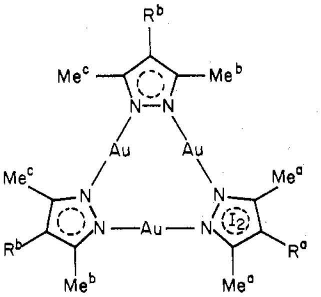
3-Me-4,5-$(CH_2)_3$-pz affording the compounds XIII, XIV, XV, and XVI, respectively. The brown solids were obtained in good yield, and their composition was established by means of elemental analysis. The compounds are indefinitely stable at room temperature, while at 100 °C (water aspirator) thermal decomposition of XIII occurs, and, after sublimation of a violet, volatile fraction (iodine), the starting pyrazolato $(3,5\text{-}Me_2\text{-}pz)_3Au_3$ (II) was recovered quantitatively. In chloroform solution the compounds are stable: in the visible spectra of their solutions no maximum was found at or around 520 nm, where the absorption of free iodine is expected.

Attempts to extend the adduct formation to other halogens (e.g., bromine) or to other metal pyrazolates have failed under the same conditions. For example, the insoluble, polymeric silver(I) 3,5-dimethylpyrazolate[31] reacts immediately with iodine in chloroform according to the reaction

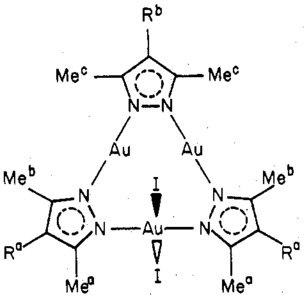
$$(1/n)[Ag(3,5\text{-}Me_2\text{-}pz)]_n + I_2 = AgI + 3,5\text{-}Me_2\text{-}4\text{-}I\text{-}pzH$$

Here the complex is broken, and the pyrazole is no longer coordinate to silver.

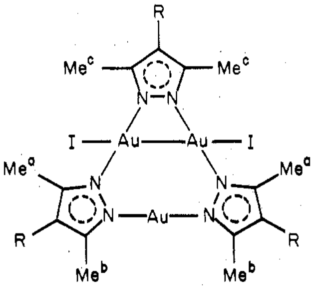
In principle, three simple structures are possible for the iodine adducts, namely, type D, a charge transfer (CT) complex involving an aromatic ring of a pyrazolato anion, type E, a mixed valence gold(I)–gold(III) derivative, and type F, a structure with a metal–metal bond.



D



E



F

In the visible spectra in chloroform solution, maxima are observed at 420–430 nm (ϵ ranging from 3000 for XV to ca. 6000 for the others) (Table II).[44] These values should be compared with the values reported for the free iodine in aromatic hydrocarbons,[32,33] where CT complexes are known to be present. In aromatic solvents the blue shift amounts to 10–30 nm only (ϵ 1000), while in our complexes the shifts are bigger (ca. 100 nm) and comparable with those found for free iodine in solvents with oxygen, sulfur, or nitrogen as the donor atom (470–410 nm; ϵ 700–4000).[32,33] In the hypothesis of a CT complex a very strong bond should be formed if the relationship[34] between the blue shift of the visible iodine band and the enthalpy of formation of the complex is accepted, $\Delta H°$ amounts to −7.3 kcal/mol for our compounds, against less than −2 kcal/mol for the adduct with benzene or with naphthalene.[34] This rather high value of $\Delta H°$ would account for the isolation of the $Au_3(pz)_3I_2$ compounds in the solid state at room temperature: indeed, other iodine adducts which were actually isolated include $R_2S{\cdot}I_2$ and $py{\cdot}I_2$ for which the reported values of $\Delta H°$ lie in the range −5 to −8 kcal/mol. In the hypothesis of a gold(I)–gold(III) complex, E, the visible spectrum is comparable to that of another compound which can only be a mixed-valence compound.[35]

The infrared spectra (4000–250 cm^{-1}) of $Au_3(pz)_3I_2$ are similar to those of the parent compounds $Au_3(pz)_3$ thus suggesting that the two types of compounds are not very different.

The proton NMR spectra of the iodine adducts in $CDCl_3$ solution are reported in Table III. They show that the symmetry of these molecules is lower than that of the starting materials $Au_3(pz)_3$ (e.g., IV), where the substituents in position 3 or 5 as well as those in 4 are all magnetically equivalent, independent of the ring to which they are connected. In the $Au_3(pz)_3I_2$ compounds XIII and XIV the rings are no longer equivalent, three sets of methyl groups (Me^a, Me^b and Me^c) being observed. A direct comparison between the starting complex and the adduct is possible only for the $Au_3(pz)_3$ and $Au_3(pz)_3I_2$ couple, where $pz^- = 3,5\text{-}Me_2\text{-}4\text{-}Et\text{-}pz^-$, owing to the insufficient solubility of the gold(I) derivatives of other symmetric pyrazolates. Upon adduct formation, only one set of methyl signals is shifted (downfield) significantly (0.35 ppm), while all the signals due to the 4-CH_3CH_2 protons are not shifted in a comparable way (≤0.15 ppm); moreover, all the three sets of CH_3CH_2 protons are displaced by the same amount. These data suggest that the compounds $Au_3(pz)_3I_2$ are mixed-valence compounds rather than charge-transfer complexes, D, at least in $CHCl_3$ solution. Indeed, if they were CT complexes, the shifts of the signals on passing from $Au_3(pz)_3$ to $Au_3(pz)_3I_2$ should affect not only the signals due to the methyl groups in the 3- or 5-position but also the signals due to the 4-CH_3CH_2 (in the compound $Au_3(3,5\text{-}Me_2\text{-}4\text{-}$

Et-pz)$_3$I$_2$) of the ring from which π donation into the σ^* orbital of the iodine should take place: the required shift is not observed.

A structure like F, analogous to that established in the $[R_2P(CH_2)(CH_2)]_2Au_2X_2$ compounds,[36] fits all the available data but seems less likely because the calculated Au–Au distance in the planar $Au_3(pz)_3$ molecule (ca. 3.4 Å) is too large to allow a regular bond between the two metal atoms.

Finally, rather unusual formulas such as $Au_3(pz)_3 \cdot {}^2/_3I_3$, analogous to those established recently for other iodine "adducts",[37,38] are excluded by the value of the conductivity in the solid state, approximately 10^{-7} Ω^{-1} cm^{-1}.[39]

The reaction of a chloroform suspension of gold(I) 3,5-dimethylpyrazolate, II, with excess 1,3,5-trinitrobenzene afforded a yellow 1:1 adduct, XIX, so unstable in solution that no reliable measurement could be carried out. Similar adduct formation was attempted with other acceptor molecules, such as tetracyanoethylene or benzoquinone, but no new compound was isolated. The adduct XIX analyzed correctly and showed all the infrared bands required by the two components plus a medium intensity band at ca. 1080 cm^{-1}. The compound is likely to be a CT complex.[40,41] In this hypothesis a π MO of the $Au_3(pz)_3$ molecule should be available for the adduct formation, the *n* electrons of the nitrogen atoms being already engaged in the robust enneaatomic ring. It is known,[42] however, that in coordination chemistry there are only a few adducts where donation takes place from a π MO.

In conclusion, the gold(I) pyrazolates show a remarkable reactivity: in particular, with three different acceptors they give three different types of reactions. With a π acceptor such as trinitrobenzene a CT complex is obtained where the pyrazolato group is the most likely electron donor; with ICl the reaction of the coordinated ligand (2) is observed; with iodine, compounds are obtained for which a mixed-valence structure is tentatively suggested, in the absence of Mössbauer or ESCA data.[43]

Experimental Section

The compounds obtained, the analytical data, molecular weight determinations, and selected infrared absorptions are reported in Table I,[44] electronic spectra in Table II,[44] and proton NMR data in Table III. Evaporation was always carried out under reduced pressure (water aspirator).

Pyrazole (Merck), benzo-1,2,3-triazole (Baker), and 1,2,4-triazole (Schuchardt) were commercial products, while 3,5-dimethyl-,[45] 3-methyl-5-phenyl-,[46] 3,5-dimethyl-4-ethyl-,[47] 3,5-dimethyl-4-iodo-,[48] 3,5-dimethyl-4-nitro-,[48] 3,5-dimethyl-4-(*p*-tolylazo)-,[49] and 3-methyl-4,5-trimethylenepyrazole[50] were prepared according to the literature methods.

Reaction 1. A solid azole, e.g., 3-methyl-5-phenylpyrazole (225 mg, 1.42 mmol) and then potassium hydroxide (82 mg, 1.47 mmol) in methanol (8 mL) were added to a stirred suspension of Me_2SAuCl (372 mg, 1.26 mmol) in the same solvent (30 mL). After the solution was stirred for 20 min, the white precipitate which formed was filtered and dissolved in benzene (ca. 100 mL). Upon addition of petroleum ether (bp 40–70 °C) to the extract, the colorless compound III (273 mg, 61%) was isolated by concentration to a small volume.

The crude compounds I, II, IV, VI, VII, VIII, IX, and X were prepared similarly. Purification was accomplished as follows: I and II were extracted and recrystallized as quickly as possible from boiling pyridine; IV was recrystallized from benzene/petroleum ether; VI was washed liberally with 80% aqueous methanol and then with pure methanol; VII was extracted with toluene in a Soxhlet apparatus until colorless extracts were obtained (4 days); VIII was precipitated by adding methanol to a chloroform extract; IX and X were washed liberally with methanol and then with ether.

Reaction 2. To a chloroform suspension (30 mL) of $Au_3(3,5\text{-}Me_2\text{-}pz)_3$ (297 mg, 0.339 mmol) was added iodine chloride (192 mg, 1.19 mmol) in the same solvent (6 mL). A brown-red solution formed at once and a white precipitate after 10 min. After 4.5 h a white precipitate (281 mg) was collected by filtration and washed by stirring under diethyl ether.

Reaction 3. To a methanol (50 mL) suspension of Ph_3PAuCl (532 mg, 1.08 mmol) were added 3,5-Me$_2$-4-NO$_2$-pz (167 mg, 1.19 mmol) and then potassium hydroxide (75 mg, 1.34 mmol) in the same solvent (ca. 10 mL). The solution was evaporated to dryness, and the residue was extracted with benzene (100 mL) in the presence of a trace of triphenylphosphine. The extract was evaporated to dryness to afford an oil which solidified by scratching under hexane. The colorless powder was extracted in a Soxhlet apparatus with boiling hexane (10 days). Both the residue and the precipitate obtained on cooling of the hexane extracts have the same analysis, spectrum, and melting point: compound XI.

The benzotriazolato XII was prepared similarly and was isolated by addition of petroleum ether to the chloroform extract; it was crystallized by dissolving in the minimum volume of $CHCl_3$ and adding hexane until incipient precipitation; upon concentration white crystals of XII were obtained. It is insoluble in alkanes; e.g., none of the complex dissolved during 3 days of Soxhlet extraction with hexane.

Reactions 3 + 4. To a methanol (100 mL) suspension of Ph_3PAuCl (2.26 g, 4.57 mmol) were added 3,5-Me$_2$-pzH (504 mg, 5.25 mmol) and then potassium hydroxide (316 mg, 5.6 mmol) in the same solvent (30 mL). The clear solution was evaporated to dryness, and the residue was extracted with benzene (150 mL) containing a small quantity of triphenylphosphine. The benzene solution was evaporated to dryness, and the residue thus obtained was extracted in a Soxhlet apparatus with boiling hexane for 3 days. Concentration of the hexane solution gave Ph_3P (infrared and melting point), while the white, insoluble product was identified as II by its analysis and infrared spectrum.

Compound V was prepared similarly, and Ph_3P was removed by Soxhelt extraction with boiling hexane (30 days). Compound VII was purified by evaporating the benzene extract to dryness; the residue was solidified by scratching under petroleum ether, and this product was purified again by Soxhlet extraction with boiling toluene. The extract on cooling gave the analytical sample of VII.

Reaction 5. (a) To a solution of compound XI (290 mg, 0.48 mmol) in methanol (30 mL) was added 50% aqueous fluoboric acid (0.7 mmol) in the same solvent (1 mL). After 10 min the filtrate was concentrated to a small volume, and diethyl ether was added: the white compound XVII (238 mg) precipitated out and was recrystallized by dissolving in a minimum volume of CH_2Cl_2 and adding ether until incipient crystallization.

(b) Silver fluoborate (0.2 g, 1.02 mmol) was added under stirring to a benzene solution (30 mL) of compound XI (312 mg, 0.52 mmol). After 3 h the suspension was evaporated to dryness, and the residue was extracted with chloroform. The solvent was removed from the extract, and the residue was solidified by scratching and purified by washing first with petroleum ether and then with diethyl ether. The white powder was recrystallized by dissolving in the minimum volume of $CHCl_3$ and adding ether until incipient crystallization. At 18 °C a 6.7×10^{-4} M acetone solution gave $\Lambda = 133$ Ω^{-1} cm^2 mol^{-1}. In the infrared spectrum a strong band centered at ca. 1050 cm^{-1} was assigned to the BF_4^- anion having T_d symmetry.

Reaction 6. The complex $[(CO)_2RhCl]_2$ (115 mg, 0.3 mmol) dissolved in benzene (25 mL) was added to a benzene solution (20 mL) of XI (310 mg, 0.52 mmol). After 30 min the solution was concentrated to a small volume; upon addition of hexane, a white precipitate was obtained which was identified as Ph_3PAuCl (C,H analysis and infrared spectrum). Upon further concentration of the mother liquor and the addition of hexane, a yellow product, XVIII (ca. 50 mg), was obtained. In the infrared spectrum terminal CO stretching modes were observed at 2080 and 2010 cm^{-1} (Nujol).

Reaction 7. To a stirred suspension of II (418 mg, 0.478 mmol) in chloroform (30 mL) was added dropwise a solution of iodine (239 mg, 0.94 mmol) in the same solvent (25 mL). The filtered solution was evaporated to dryness. The residue was washed several times with petroleum ether (350 mL) and stirred overnight with the same solvent (50 mL) which was removed by decantation. The residue was dissolved in chloroform; a small amount of petroleum ether (5 mL) was added; a small quantity of white precipitate was filtered away and identified as II by its infrared spectrum and elemental analysis. On concentration and further addition of petroleum ether, the product, XIII, was obtained as a brownish red precipitate. The compound has no definite melting point; in air decomposition begins at ca. 115 °C, the sample turning whitish. The infrared data are given in the supplementary material. The ^{13}C NMR spectrum (25.2 MHz, 28 °C, CDCl$_3$ solution) was recorded for 2 days, some gold being present in the NMR tube at the end of this time. The chemical shifts were found at 13.84, 13.28, and 12.97 (methyls), at 106.67 and 104.0 (CH groups), and at 151.57 and 148.17 (C–N) ppm from Me_4Si. The assignments were checked by running the same spectrum without proton decoupling.

Compounds XIV, XV, and XVI were obtained similarly, by addition of hexane to the concentrated dark red solution of the reagents in the stoichiometric ratio or, also, with an excess of iodine. The infrared data are given in supplementary material.

Trinitrobenzene Adduct, XIX. To a stirred suspension of II (103 mg, 0.12 mmol) in chloroform was added symmetric trinitrobenzene (235 mg, 1.10 mmol) in the same solvent (10 mL in all). After overnight stirring, a violet suspended material was removed by filtration. The solution was slowly concentrated (ca. 4 mL); upon addition of diethyl ether (20 mL) the yellow product was precipitated, washed with ether, and analyzed. The compound had no definite melting point; it looked white at 175 °C, blackened from 210 °C, and was violet at ca. 255 °C. Infrared spectral data can be found in the supplementary material.

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Registry No. I, 68630-73-9; II, 52707-27-4; III, 52707-09-2; IV, 52707-28-5; V, 68630-59-1; VI, 68630-60-4; VII, 68630-61-5; VIII, 68682-84-8; IX, 68630-52-4; X, 39394-95-1; XI, 68630-58-0; XII, 68630-54-6; XIII, 68630-62-6; XIV, 68630-63-7; XV, 68715-76-4; XVI, 68630-53-5; XVII, 68630-65-9; XVIII, 68630-66-0; XIX, 68867-05-0; Me_2SAuCl, 29892-37-3; Ph_3PAuCl, 14243-64-2; $[(CO)_2RhCl]_2$, 14404-25-2.

Supplementary Material Available: Listings of the analytical data, molecular weight determinations, and selected infrared absorptions (Table I), visible spectra (Table II), and the principal absorptions in the infrared spectra of compounds XIII, XIV, and XIX (4 pages). Ordering information is given on any current masthead page.

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